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THE ELEMENTS
OF
PHYSICAL CHEMISTRY

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THE ELEMENTS OF PHYSICAL CHEMISTRY

BY

HARRY C. JONES

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JOHNS HOPKINS UNIVERSITY

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PREFACE

It is now generally known that within the last fifteen years a new branch of science has come into existence. This branch, occupying a position between physics and chemistry, is known as physical chemistry. The term, however, is by no means a new one. We have had physical chemistry since the beginning of the last century. In order to distinguish the new science from the old, from which it differs in kind, it has been termed the new physical chemistry.

There seems to be a tendency in the last few years to ignore the work of the older physical chemists, and to regard that physical chemistry which is of any value as dating not earlier than 1885. To any one who holds this view, this work will seem to lay undue stress upon, and devote an unnecessary amount of space to the older work.

It, however, appears to the writer that in order to appreciate the gigantic strides made by the new physical chemistry, it is not necessary to reject, or even ignore the work of such men as Kopp, Bunsen, Gladstone, Regnault, and the other great founders of chemical and physical science. If we would study their work more closely, we would see that it lies at the foundation of much that has been developed within the last few years.

It has been the aim of the author to deal with the whole subject of physical chemistry in an elementary manner. The rapidly increasing desire, on the part of students of chemistry and physics, to know more of physical chemistry is manifesting itself in every direction. It is with the object of helping such students in the later stages of their college work and in the earlier part of their university career that this work has been prepared.

The question might be raised that if this is meant to be an elementary text-book, why is so much presupposed? No one can use this book successfully without an elementary knowledge of physics, of chemistry, and of mathematics. The answer is that this is partly inherent in the nature of the subject. Physical chemistry involves at least the elements of physics, and of chemistry inorganic and organic; and the student must also be familiar with the elementary calculus if he would go deeply into the subject, and it would be well to add the elements of thermodynamics and differential equations. It is, however, true that much may be learned about physical chemistry without any knowledge of the higher mathematics; but such information must always be more or less unsatisfactory.

In reference to the contents of that portion of the work which deals with the newer physical chemistry, a few words should be added in this connection. The new physical chemistry really begins with the chapter on solutions, and this is one of the most important chapters. The discovery of the relations between dilute solutions and gases has placed the subject of solutions at the very foundation of the new developments in physical chemistry.

The subject of thermochemistry, while important and interesting, has never acquired that prominence which, for a long time, it seemed likely to attain, partly because the data are often so complex that it is difficult to interpret them and discover their meaning.

Electrochemistry, on the other hand, is of the very greatest importance. In no chapter of physical chemistry have greater advances been made in recent time, and nowhere do we find experimental work of greater value.

The study of chemical dynamics and statics has been very much to the front ever since the recognition of the importance of the law of mass action. It will be observed that reaction velocities, and equilibrium in chemical reactions have been dealt with from the standpoint of this law. This appeals to the author as being the most exact and by far the simplest method of treating these problems. The phase rule, however, is considered at sufficient length, and applied, it is hoped, to a sufficient number of cases to make clear this important generalization.

An attempt has been made to prepare a balanced work. The danger of treating certain subjects too fully and of following certain deductions beyond the scope of the remainder of the book has been felt, and an earnest endeavor has been made to avoid this defect.

In dealing with the older as well as with the newer work the author has endeavored to obtain his information from original articles wherever it was possible, and in most cases it has been possible. He, however, wishes to express his indebtedness especially to Lothar Meyer's *Die modernen Theorien der Chemie*, to Ostwald's great *Lehrbuch der allgemeinen Chemie*, to Nernst's *Theoretische Chemie*, and to Van't Hoff's *Vorlesungen über theoretische und physikalische Chemie* for references to the literature. These have made it a much simpler matter to find just what was desired at any moment.

Little need be said at this date in reference to the importance of the whole subject of physical chemistry. It has already extended into nearly every field of chemical science, contributing largely to the interpretation of phenomena hitherto not understood. It has thrown light on so many problems in chemistry that it has now become an integral part of that science. And it is recognized that no chemist to-day, scientific or technical, can omit physical chemistry without losing an essential part of his training.

Physical chemistry has also thrown light on a number of physical problems, especially in connection with the study of primary cells, as we shall see when we study electrochemistry.

It has also reached out into biology, and has become essential to the physiologist and pharmacologist. This has been shown by the work of Loeb, Dreser, and others. And that physical chemistry is to find its way into the geological sciences has become obvious from the work of Van't Hoff in the last two or three years. The wide-reaching significance of the subject would account for its almost unprecedented growth in the last decade and a half of the nineteenth century.

HARRY C. JONES.

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THE ELEMENTS OF PHYSICAL CHEMISTRY

CHAPTER I

ATOMS AND MOLECULES

THE ATOMIC THEORY

The Law of the Conservation of Mass. — The study of chemical phenomena, like the study of natural phenomena in general, was at first purely qualitative. It was early observed that when certain substances are brought together they react, giving rise to new substances, and it was also noted that the substances formed as the result of the reaction have many properties which are very different from those of the substances from which they were formed. These qualitative observations, however, while absolutely necessary in the earlier stages of any branch of science, are far from sufficient. The mere fact that from certain things other things are formed is not only empiricism, but empiricism in the earliest stage; since it is but the result of the observation of the more superficial side of the phenomenon of chemical activity, and entirely lacks any quantitative basis. The qualitative stage is followed, wherever it is possible, by the quantitative; and so it has been in chemistry. Known quantities of substances were used, and the amounts of the substances formed determined. Almost as soon as chemists began to work with known masses of substances, the remarkable fact was discovered that in chemical transformations mass remains unaltered. This is remarkable because it is the only property which remains unchanged in chemical reaction. When two or more substances react, nearly all of the properties of the products of the reaction are different from those of the substances which enter into the reaction. This is well illustrated by the reaction between metallic sodium and chlorine, resulting in the formation of sodium chloride. The salt formed has properties very different from either constituent.

Indeed, all of the most striking properties of both constituents are lost during the reaction. Yet, in the midst of all this change of properties which takes place in chemical reactions, the one property, mass, stands immutable.

We measure mass by weight, and are accustomed to say that in chemical reactions weight remains unchanged; the weight of all the products of the reaction, under the same conditions, is exactly equal to the weight of all the substances which enter into the reaction. This is true; but since weight is but a measure of mass, it is the conservation of the mass and not of the weight upon which we should fix our attention.

This law of the conservation of mass is sometimes referred to as the law of the conservation of matter. The former expression is greatly to be preferred to the latter, since it states just what we have established by experiment. The latter goes far beyond the facts and, as Ostwald has pointed out, is pure theory.

The question as to whether there is any change in weight in chemical reaction has recently been thoroughly investigated by Landolt.[1] In his work the most refined balances which have ever been made were employed; and in every detail the work is a classic for thoroughness and accuracy. While certain small changes in weight were observed, yet in no case was the difference sufficient to justify the conclusion that there is any change in weight in chemical reaction.

The Law of Constant Proportion. — The second important generalization which was reached through the quantitative study of chemical phenomena, was that the constituents of a chemical compound are always present in a constant proportion. If two substances unite and form a third, they enter into combination in a constant proportion by mass. The law may be stated thus: —

Every chemical compound always contains the same constituents, and there is a constant proportion between the masses of the constituents present.

The law of constant proportions was called in question in the early years of this century by Berthollet.[2] He was impressed by the effect on the chemical reaction of the quantity of substance used, and saw in outline what has since been established as the law of mass action. He thought that not only the nature and magnitude of the reaction were affected by the masses of the substances used, but also the composition of the products formed. Two substances could unite in a great many proportions, and the composition of the product depended chiefly on the relation between the amounts of the substances used.

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[1] *Ztschr. phys. Chem.* **12**, 1 (1893).

[2] *Essai de statique chimique* (1803).

The error of Berthollet was corrected by Proust, who showed that many of the substances which were supposed by Berthollet to be compounds were simply mixtures. The result of the most accurate investigations is to show that the law of constant proportions is a fundamental law of chemical reaction.

Law of Multiple Proportions. — While it is true that substances combine in constant proportions, it is also true that two substances may combine in more than one proportion. Dalton[1] examined the two compounds, methane and ethylene, and found that the ratio of carbon to hydrogen in the former was as 3 to 1; in the latter as 6 to 1. The latter compound evidently contains twice as much carbon with respect to hydrogen as the former. Similarly, there is just twice as much carbon with respect to oxygen in carbon monoxide as in carbon dioxide. A large number of other compounds were examined, in which simple ratios between the masses of the constituents were discovered. From these and similar facts Dalton arrived at the law of multiple proportions, which may be stated thus: —

If two substances combine in more than one proportion, the masses of the one which combine with a given mass of the other, bear a simple rational relation to one another.

The Law of Combining Weights. — There is a third law to which the masses of substances which combine with one another conform. This has been termed the law of combining weights. If we determine the weights of different substances which combine with a given weight of a definite substance, these weights, or simple multiples of them, represent the quantities of the different substances which will combine with one another. The quantities of substances which combine with one another have been termed their *combining numbers.*

Substances combine either in the ratio of their combining numbers, or in simple rational multiples of these numbers.

This law, like the laws of constant and multiple proportions, has been subjected to the most careful experimental test, and has been shown to be true to within the limit of error of some of the most refined experimental work.

Origin of the Atomic Theory. — The discovery of empirical relations, such as the three laws of chemical combination just considered, is of great importance, and is absolutely essential to scientific progress; but these are chiefly of interest as they lead to correct theories and wide-reaching generalizations. Dalton raised the question, What does the law of multiple proportions really mean? Why do such relations obtain? His answer is what has come to be known as the scientific atomic theory, in contradistinction to the older imaginative speculations about atoms and molecules. The view that matter is composed of indivisible particles or atoms, which have definite weights, and that chemical action takes place between these particles, was to Dalton the only rational explanation of the laws of multiple proportion and combining weights. If matter is composed of such ultimate parts or atoms, then a constant number of atoms of one substance combine with one atom of another substance to form a definite compound, and we have the law of constant proportions. One atom of one substance may combine with one atom of another substance, or a number of atoms of one substance may combine with one of another; but the number must be a simple rational whole number; whence the law of multiple proportions.

---

[1] *New System of Chemical Philosophy* (1808).

Since the atoms have definite weights, and the laws of constant and multiple proportions are true, the law of combining numbers follows as a necessary consequence of the atomic theory. And, further, if the same number of atoms of the two substances combine, the combining numbers represent the relative weights of the atoms which enter into combination. This furnished a means of determining the relative atomic weights.

DETERMINATION OF RELATIVE ATOMIC WEIGHTS

Combining Numbers and Atomic Weights. — The problem of determining the relative weights of atoms seems at first sight a very simple matter, from what was stated above. It is only necessary to determine the relative weights of substances which combine — the combining numbers — in order to find out the relative weights of the atoms of these substances. This would be true if a given number of atoms of one substance always combined with an equal number of atoms of another. But we know that this is not the case, since it often happens that two elementary substances combine in several proportions. To determine the relative atomic weights of the elements, we must, therefore, know the combining numbers of the elements, and also the number of atoms of the different elements which combine with one another. We will take up first the method of determining the combining numbers of the elements.

Chemical Methods of determining Combining Numbers. — The simplest method would be to take some element as our standard, and call its combining number one. Then allow all of the other elements to combine with this one, and determine the weights of the different elements which combined with unit weight of our standard element. Since hydrogen has the smallest combining number, it would naturally be chosen as the unit. The problem then would be to determine, say, the number of grams of the different elements which combine with one gram of hydrogen, and these figures would represent the combining weights of the elements in terms of hydrogen as unity. Since it is true that comparatively few of the elements combine directly with hydrogen, the direct comparison with hydrogen cannot be made in many cases.

A large number of the elements, however, combine directly with oxygen. We can determine the ratio between the combining numbers of these elements and oxygen, and then the ratio between the combining number of oxygen and that of hydrogen, and thus calculate the combining numbers of the elements in terms of our unit hydrogen.

We might thus work out a table of the combining numbers of all of the elements in terms of hydrogen as unity. This part of the problem is, however, not as simple as would be indicated from the above. Many of the elements combine in more than one proportion. Take the case of hydrogen and carbon. The combining number of carbon in terms of hydrogen as unity would be 3 if determined by the analysis of marsh gas. From the analysis of ethylene we would conclude that it was 6, while from the analysis of acetylene it would appear to be 12. A similar complexity would result in the case of carbon and oxygen. If we take oxygen as 16 in terms of hydrogen 1, the combining number of carbon, as determined from carbon monoxide, would be 12, while as determined from carbon dioxide it would be 6. We would thus obtain different combining numbers for the same element, depending upon which of its compounds we selected.

It is perfectly clear that neither the chemical analysis of the compound, nor its synthesis from the elements, throws any light on the problem as to the number of atoms of one substance combined with one atom of the other. Berzelius attempted to solve this part of the problem of atomic weights by means of certain dogmatic rules, which have only this value, that they brought out a large amount of experimental work which resulted in new and improved methods of analysis. Chemical methods alone can lead only to the combining weights or numbers of the elements, and, as already stated, in many cases more than one combining weight for an element would be obtained. Other methods must be employed in order to determine the number of atoms of the one element which have combined with one atom of the other. To these we will now turn.

Molecular Weights determined from the Densities of Gases. — Gay Lussac[1] showed in 1808 that the densities of gases are proportional to their combining weights, or to simple rational multiples of them. If two gases react chemically, the volumes which react are either equal, or bear a simple rational relation to one another. And, further, if the product formed is a gas, its volume bears a simple rational relation to the volumes of the gases from which it was formed. Thus, one volume of hydrogen combines with one volume of chlorine, and forms two volumes of hydrochloric acid gas. One volume of oxygen combines with two volumes of hydrogen, forming two volumes of water-vapor. One volume of nitrogen combines with three volumes of hydrogen, forming two volumes of ammonia.

From the laws of definite and multiple proportions, the law of combining numbers, and the atomic theory which was proposed to account for these, we see that every chemical reaction takes place between a definite number of atoms, and the number is usually small. Therefore, the discovery of Gay Lussac leads to the conclusion that —

The number of atoms contained in a given volume of any gas must bear a simple rational relation to the number of atoms contained in an equal volume (at the same temperature and pressure) of any other gas.

We have thus far, however, no means of determining the numerical value of this relation, and, therefore, cannot use the discovery of Gay Lussac alone to determine relative atomic weights.

Avogadro's Hypothesis. — Avogadro[2] in 1811, taking into account all of the facts known, advanced the hypothesis that —

In equal volumes of all gases, at the same temperature and pressure, there is an equal number of ultimate parts or molecules.

Avogadro extended his hypothesis to all gases, including even the elementary gases, and regarded the molecules of these substances as made up of atoms of the same kind, which had united with one another. This was a necessary consequence of his hypothesis. One volume of hydrogen gas combines with one volume of chlorine gas, and forms two volumes of hydrochloric acid gas. If there are the same number of molecules in equal volumes of all gases, there would be twice as many in the two volumes of hydrochloric acid as in the one volume of hydrogen, or the one volume of chlorine. Since each molecule of hydrochloric acid must contain at least one atom of hydrogen and one atom of chlorine, the molecule of hydrogen and of chlorine must be made up of at least two atoms. Ampère,[1] in 1814, advanced essentially the same hypothesis as had been proposed three years before by Avogadro. The hypothesis of Avogadro has been confirmed by such an abundance of subsequent work, in so many directions, that it is now placed among the well-established laws of nature. It points out distinctly the difference between atoms and molecules, and rationally explains why different gases should obey the same law of volume and of pressure, and have the same temperature coefficient of expansion. It has been tested from both the physical and mathematical standpoints, and now lies at the basis of much of our knowledge of gases.

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[1] *Mém d. Arcueil*, T., II. (1808).

[2] *Journ. de Phys.* **73**, 58–76 (1811).

Avogadro's Hypothesis and Molecular Weights. — Given the hypothesis of Avogadro, the determination of the relative molecular weights of gases is very simple. If there is an equal number of molecules contained in equal volumes of the different gases, the relative weights of equal volumes of these gases give at once the relative weights of the molecules contained in them. It is only necessary to choose some substance as our standard, and express the molecular weights of other substances in terms of this standard. We would naturally select as the unit that substance which has the smallest density, and this is hydrogen. From what has been said, however, in reference to the union of hydrogen and chlorine, forming hydrochloric acid, it is certain that the molecule of hydrogen contains at least two atoms. We will, therefore, call the molecular weight of hydrogen two, and calculate the molecular weights of other elements in terms of this standard. The densities of substances are usually determined in terms of air as the unit. It is a simple matter to recalculate these in terms of hydrogen as two. The density of hydrogen in terms of air as the unit is 0.06926.[2] We must multiply this by 28.88 to obtain our new unit two

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[1] Lettre de M. Ampère à le Berthollet, *Ann. de Chim.* **90**, **43.**

[2] Later determinations give 0.0696.

($2 \div 0.06926 = 28.88$). Similarly, for other substances whose densities are known with reference to air; these densities must be multiplied by the constant 28.88 to transform them into densities in terms of hydrogen = 2. These latter values are the relative molecular weights of the substances in the form of gas, referred to the molecular weight of hydrogen as two. A few results are given in the following table, showing in column I the densities in terms of air as the unit; in column II the densities or relative molecular weights in terms of hydrogen = 2. The results in column II are obtained by multiplying the results in column I by 28.88.

	I		II
Hydrogen, 0° C.	0.06926	× 28.88	2
Oxygen, 0° C.	1.10563		31.93
Nitrogen, 0° C.	0.9713		28.05
Sulphur, 1400° C.	2.17		62.67
Chlorine, 200° C.	2.45		70.75
Bromine, 100° C.	5.54		159.99
Mercury, 1400° C.	6.81		196.67
Iodine, 940° C.	8.72		251.83

The molecular weights of compounds can be determined in exactly the same manner from the densities of their vapors. If these have been determined on the basis of air as unity, we must multiply by 28.88 to obtain the molecular weight referred to hydrogen as two. The molecular weights of compounds thus obtained must bear a rational relation to the combining weights of the elements which enter into the compound. The molecular weights as obtained from vapor-densities can, therefore, be corrected by the most careful analytical or synthetical determination of the combining weights of the elements which enter into the compounds.

Atomic Weights from Molecular Weights. — If we knew the number of atoms contained in the molecule of elements in the gaseous state, the problem of relative atomic weights would be solved at once by dividing the molecular weight of the gas by the number of atoms in the molecule. The problem is, however, not as simple as this, since we do not know at once the number of atoms in the molecules of elements. Other lines of thought have enabled us to solve this the second part of our problem.

The definition of an atom as an indivisible particle of matter shows that fractions of atoms cannot exist. No molecule can contain a fraction of any atom. The quantity of any substance which enters into a molecule must be at least one atom. It may be more than one, but it cannot be less. This is the key to the problem. Suppose we wish to determine the number of hydrogen atoms in a molecule of hydrogen. We must examine compounds into which hydrogen enters, and find out what is the smallest quantity of hydrogen which enters into the molecule of the compound. Let us take hydrochloric acid, whose molecular weight is 36.45. This is shown by analysis to be composed of 1 part of hydrogen and 35.45 parts of chlorine. This 1 part of hydrogen is at least one atom; it may be more, but it cannot be less. By examining a large number of compounds into which hydrogen enters, it has been found that hydrogen never enters into a molecule of any substance in a smaller quantity than in hydrochloric acid. This is, therefore, for us the atom of hydrogen, but it may in reality be composed of a great number of smaller parts. The hydrogen which enters into the molecule of hydrochloric acid is just half the quantity which forms the molecule of hydrogen gas, since one volume of hydrogen combining with one volume of chlorine yields two volumes of hydrochloric acid gas. The molecule of hydrogen, therefore, contains at least two atoms, and since there is no experimental reason for assuming that it contains more than two, we say that the molecule of hydrogen is made up by the union of two hydrogen atoms. Knowing the number of atoms in the molecule, the atomic weight follows at once from the molecular weight determined by vapor-density, and corrected by the most refined methods of chemical analysis.

By methods similar to the above the molecules of many elements have been shown to be composed of two atoms. But this by no means applies to all elementary substances. The molecules of some elementary substances contain more than two atoms, and in a very few cases the molecule and atom seem to be identical. And, further, the number of atoms contained in the molecule has been shown to vary in some cases with change in conditions, especially with change of temperature. But by studying a large number of compounds of an element, and ascertaining what is the smallest quantity of the element which ever enters into a compound, we can determine the number of atoms contained in a molecule of the element itself. Knowing the number of atoms in the molecule of the element, and the weight of the molecule, we can determine relative atomic weights. The relations between the molecular weights of a few of the elements and their atomic weights are given in the following table: —

Elements	Atomic Weights	Molecular Weights
Hydrogen	1	2
Nitrogen	14.01	28.02
Oxygen	15.88	31.76
Phosphorus	30.96	123.84
Sulphur	31.98	63.96 above 800° C. 191.88 at 500° C.
Chlorine	35.18	70.36
Arsenic	74.9	299.6
Selenium	78.9	157.8
Bromine	79.34	158.68
Cadmium	111.7	111.7
Tellurium	126.3	252.6
Iodine	125.89	251.78 under 600° C.
Mercury	199.8	199.8

This table brings out a number of facts to which reference has already been made. The molecular weight of a number of the elements is twice as great as the atomic weight. In some cases, as with sulphur, the molecular weight is twice the atomic weight at a given temperature, and then varies with the temperature. In the cases of cadmium and mercury the molecular weights are apparently identical with the atomic weights. This matter will be taken up later in other connections.

It frequently happens that an element boils at such a high temperature that we cannot determine accurately its vapor-density. In such cases volatile compounds of the element are used, and their molecular weights determined. These compounds are then analyzed, and the one containing the smallest quantity of the given element in its molecule is said to contain one atom of the element. The real atom of the element may be a fraction of this quantity, but this is for all chemical or physical chemical purposes the atom, and its relative weight is the atomic weight of the element in question.

Atomic Weights from Specific Heats. — Dulong and Petit[1] in 1819 showed that a very simple relation exists between the specific heats of elements in the solid state and their atomic weights. They found that the specific heats varied inversely as the atomic weights, and, consequently, that the product of the specific heats and atomic weights of the elements is a constant. This will be seen from the following data: —

shows

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[1] Ann. Chim. Phys. 10, 395 (1819).

	Specific Heat	Atomic Weight	Product
Lithium	0.941	7.01	6.6
Sodium	0.293	22.99	6.7
Magnesium	0.250	23.94	6.0
Potassium	0.166	39.03	6.5
Calcium	0.170	39.91	6.8
Iron	0.112	55.90	6.3
Cobalt	0.107	58.60	6.3
Nickel	0.108	58.60	6.4
Zinc	0.0932	64.9	6.1

From these and similar facts Dulong and Petit announced their law:—

The atoms of all elements have the same capacity for heat energy.

After the discovery of this law it was a comparatively simple matter to determine the atomic weights of solid elements from their specific heats. If specific heat multiplied by atomic weight is a constant, the atomic weight is equal to the constant divided by the specific heat. The numerical value of the constant, taken as the average for a number of elements, is about 6.25.

Exceptions to the law of Dulong and Petit were early recognized. Weber[1] determined the specific heats of the elements carbon, boron, and silicon, at temperatures between 0° and 100° C., and obtained much smaller values than would be expected from the law of Dulong and Petit, using the atomic weights of these elements as determined from Avogadro's law. He found, however, that the specific heats of these elements varied widely with change in temperature, and that above a certain temperature the specific heats became constant. At these elevated temperatures, where the specific heats became constant, they conformed to the law of Dulong and Petit. These constant specific heats were obtained only at comparatively high temperatures; for silicon at about 200° C., for the different modifications of carbon at about 600° C., for boron at about 500° C. The different modifications of carbon had different specific heats at low temperatures, but at elevated temperatures this difference also was found to vanish, the different varieties of carbon at red heat showing the same specific heats. Similar observations were made on glucinum by Nilson and Pettersson.[2]

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[1] *Pogg. Ann.* **154**, 367 (1875). *Ber. d. chem. Gesell.* **5**, 303 (1872).

[2] *Ber. d. chem. Gesell.* **13**, 1451 (1880).

Elements	Atomic Weights	Molecular Weights
Hydrogen	1	2
Nitrogen	14.01	28.02
Oxygen	15.88	31.76
Phosphorus	30.96	123.84
Sulphur	31.98	63.96 above 800° C. 191.88 at 500° C.
Chlorine	35.18	70.36
Arsenic	74.9	299.6
Selenium	78.9	157.8
Bromine	79.34	158.68
Cadmium	111.7	111.7
Tellurium	126.3	252.6
Iodine	125.89	251.78 under 600° C.
Mercury	199.8	199.8

This table brings out a number of facts to which reference has already been made. The molecular weight of a number of the elements is twice as great as the atomic weight. In some cases, as with sulphur, the molecular weight is twice the atomic weight at a given temperature, and then varies with the temperature. In the cases of cadmium and mercury the molecular weights are apparently identical with the atomic weights. This matter will be taken up later in other connections.

It frequently happens that an element boils at such a high temperature that we cannot determine accurately its vapor-density. In such cases volatile compounds of the element are used, and their molecular weights determined. These compounds are then analyzed, and the one containing the smallest quantity of the given element in its molecule is said to contain one atom of the element. The real atom of the element may be a fraction of this quantity, but this is for all chemical or physical chemical purposes the atom, and its relative weight is the atomic weight of the element in question.

Atomic Weights from Specific Heats. — Dulong and Petit[1] in 1819 showed that a very simple relation exists between the specific heats of elements in the solid state and their atomic weights. They found that the specific heats varied inversely as the atomic weights, and, consequently, that the product of the specific heats and atomic weights of the elements is a constant. This will be seen from the following data: —

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[1] *Ann. Chim. Phys.* **10**, 395 (1819).

	Specific Heat	Atomic Weight	Product
Lithium	0.941	7.01	6.6
Sodium	0.293	22.99	6.7
Magnesium	0.250	23.94	6.0
Potassium	0.166	39.03	6.5
Calcium	0.170	39.91	6.8
Iron	0.112	55.90	6.3
Cobalt	0.107	58.60	6.3
Nickel	0.108	58.60	6.4
Zinc	0.0932	64.9	6.1

From these and similar facts Dulong and Petit announced their law: —

The atoms of all elements have the same capacity for heat energy.

After the discovery of this law it was a comparatively simple matter to determine the atomic weights of solid elements from their specific heats. If specific heat multiplied by atomic weight is a constant, the atomic weight is equal to the constant divided by the specific heat. The numerical value of the constant, taken as the average for a number of elements, is about 6.25.

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[1] *Pogg. Ann.* **154**, 367 (1875). *Ber. d. chem. Gesell.* **5**, 303 (1872).

[2] *Ber. d. chem. Gesell.* **13**, 1451 (1880).

The law of Dulong and Petit is, in general, only approximately true, and holds only within certain limits of temperature.

The relation between the specific heats of compounds and the specific heats of their constituents was next investigated. Neumann[1] showed that equivalent quantities of analogous compounds have the same capacity for heat, and Regnault, Kopp,[2] and others pointed out the following relation between the specific heats of compounds and the specific heats of their constituents. *The capacity of the atoms for heat energy is not appreciably changed when they unite and form compounds.* In a word, the capacity of the molecule for heat is the sum of the capacities of the atoms in the molecule.

The recognition of this relation makes it possible to greatly extend the method of determining atomic weights by specific heats. Many of the elements are solids only at temperatures which are too low to be dealt with by the methods of measuring specific heats. But these elements form solid compounds with other elements whose specific heats and atomic weights can be determined. Let us take an example.[3]

Chlorine is an element whose specific heat in the solid state would be very difficult to determine. Chlorine, however, forms a solid compound with the element lead. The specific heat of lead chloride has been found by Regnault to be 0.0664; 206.4 parts of lead yield 277.1 parts of lead chloride. Multiplying this number by the specific heat of lead chloride, we obtain the molecular heat. $277.1 \times 0.0664 = 18.4$. Subtracting the atomic heat of lead, 6.5, we have 11.9 as the atomic heat, corresponding to 70.7 parts of chlorine. Since the atomic heat of the elements is about 6, we have in 70.7 twice the atomic weight of chlorine, or the atomic weight of chlorine = 35.35. This agrees very closely with the atomic weight of chlorine determined by the vapor-density method, based upon the law of Avogadro.

The above example serves to illustrate the way in which the specific heats of compounds are used to determine atomic weights. The method has been widely applied, and it may be said in general, that the atomic weights determined from the law of Dulong and Petit agree with those obtained from the law of Avogadro, although some discrepancies exist.

Isomorphism an Aid in determining Atomic Weights. — It was recognized even in the eighteenth century that substances of different composition often have the same, or very nearly the same, crystal form. This was at first explained by assuming that certain substances have the power of forcing other substances to take their own crystal form. Mitscherlich[1] interpreted this fact quite differently. He studied the salts of arsenic and phosphoric acids, and found that those which contained an equal number of atoms in the molecule had the same or very similar crystal forms. Mitscherlich concluded at first that it was only the number and not the nature of the atom which conditioned the crystal form. Later, he recognized that the way in which the atom was united in the compound was an important factor in determining its crystal form, and then arrived at the generalization that, "*An equal number of atoms combined in the same way produce the same crystal form, and that the same crystal form is independent of the chemical nature of the atoms, but depends only on their number and position.*"

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[1] *Pogg. Ann.* **23**, 1 (1831).

[2] *Lieb. Ann.* (1864), Suppl. **3**, 5.

[3] Meyer: *Die modernen Theorien der Chemie*, p. 100.

If this relation was true, it would throw much light on the number of atoms in a compound, and therefore be of service in determining atomic weights. Given two isomorphous substances such as $BaCl_2\,2\,H_2O$ and $BaBr_2\,2\,H_2O$, from the law of Mitscherlich their molecules must contain the same number of atoms. If we know the atomic weights of all of the elements in the former compound, we can find the atomic weight of the bromine in the latter substance.

This relation pointed out by Mitscherlich was accepted at once by Berzelius, who made it the basis of atomic weight determinations. The law, however, did not long remain without exceptions. Mitscherlich[2] showed that the compounds $BaMn_2O_8$, Na_2SO_4, and Na_2SeO_4 are isomorphous, and they evidently contain a very different number of atoms in the molecule. An attempt was made to overcome this difficulty by ascribing to these compounds the formulas, $BaMn_2O_8$, NaS_2O_8, and $NaSe_2O_8$, but these were so strongly at variance with all the facts known that they had to be abandoned, and a number of other substances were soon discovered to be isomorphous which could not possibly be regarded as containing the same number of atoms in the molecules.

The generalization of Mitscherlich is then only an approximation to which there are many exceptions, and this method of determining atomic weights must be used with great caution.

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[1] *Ann. Chim. Phys.* [2], **14**, 172 (1820).

[2] *Pogg. Ann.* **25**, 287 (1832).

The modifications of the law of Mitscherlich proposed by Marignac[1] and Kopp[2] have scarcely increased our confidence in it as a means of determining atomic weights. The former has shown that equality in the number of atoms in compounds is not necessary in order that we may have isomorphism, and Kopp would limit the term isomorphism to substances which will grow in each other's solutions. The application of the conception of isomorphism to the problem of atomic weights has, however, been of much service, especially in the earlier stages of such work.

Most Accurate Method of determining Atomic Weights. — The general methods described for determining the relative atomic weights of the elements differ greatly in their relative accuracy. Of these the various chemical methods for determining the constituents of compounds are by far the most accurate. Indeed, the other methods described, such as the vapor-density method, and the methods based upon specific heat of solids, and upon isomorphism, must be regarded simply as checks upon the chemical methods. By means of chemical analysis or synthesis we determine with the greatest degree of accuracy the combining weights of elements, and then make use of the other methods to decide whether we are dealing with one or more atoms.

In determining atomic weights we must choose some element as our standard. We would naturally take the lightest element, hydrogen, and call it unity. This has been done, and all atomic weights referred to this unit. But it is unfortunately true, as has been stated, that hydrogen does not combine directly with many of the elements and form stable compounds which can be analyzed.

Oxygen, on the other hand, does combine with a large number of the elements, forming some of the most stable compounds with which we are acquainted. It therefore seemed best to compare the atomic weights of the elements directly with the atomic weight of oxygen, and then compare oxygen with hydrogen, with which it forms the very stable compound, water. It should be stated, however, that this method is by no means free from objections, and many prefer retaining hydrogen as the unit. The atomic weight of oxygen, in terms of hydrogen as the unit, was supposed for a long time to be the whole number 16. If this was true, it would obviously make no difference whether we called hydrogen 1 or oxygen 16, and then compare all other atomic weights with these standards. It has recently been shown beyond question that when hydrogen is 1, oxygen is not 16, but considerably less (15.88). We must, therefore, choose between these two substances as the basis of the system of atomic weights. The majority of investigators at present seem inclined to select oxygen as the standard, taking its atomic weight as 16, and referring the atomic weights of all the other elements to this basis.

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[1] *Lieb. Ann.* **132**, 29 (1864).

[2] *Ber. d. chem. Gesell.* **12**, 909 (1879).

The most direct method of determining the combining weight of an element, in terms of oxygen as our standard, would be to determine the weight of the element which would combine with a known weight of oxygen. The combining weight of the element would then be calculated by the simple proportion, —

Wt. oxygen : wt. element = at. wt. oxygen : combining wt. element.

We should then have to determine, by some of the methods already referred to, how many atoms of the element in question combined with one atom of oxygen.

While it is true that oxygen combines directly with many of the elements, forming stable compounds, it is by no means true that it forms such compounds with all of the elements. And further, some of the elements form compounds with oxygen which are gaseous or liquid at ordinary temperatures, and for these or other reasons are not adapted to atomic weight determinations. In such cases the atomic weight of the element must be compared with that of some element other than oxygen, which in turn has been compared with oxygen. Thus, the atomic weights of the halogens have been determined in terms of the atomic weight of silver, and the latter then determined in terms of oxygen. Even more complex cases may arise, where it is necessary to compare the atomic weight of an element with the sum of the atomic weights of two or more elements, each of which has been determined in terms of oxygen.

It is evident that the more direct the comparison of the atomic weight of the element with that of oxygen, the better; since the accumulation of experimental errors, resulting from indirect comparisons, is avoided.

Some of the most refined experimental work which has ever been done has had to do with the problem of relative atomic weights. It is obviously necessary that these constants should be determined with the very greatest degree of accuracy, since all chemical analysis and much of the most refined work in physical chemistry and in physics depends upon them. In this connection we should mention, especially among the earlier work, that of Stas[1] and Marignac,[2] and among the more recent investigations those of Morley[3] and Richards.[4]

The work of Stas had to do more especially with the relations between silver and the halogens, but included, also, a large number of other elements, especially lithium, sodium, potassium, sulphur, lead, and nitrogen. The work of Stas, as a whole, has become a model for refinement and accuracy, and is simply wonderful when we consider the comparatively crude apparatus with which it was carried out.

Marignac has done an enormous amount of work on the problem of atomic weights. He has determined the atomic weights not only of chlorine, bromine, and iodine, but of carbon and nitrogen, calcium, barium, magnesium, zinc, manganese, nickel, cobalt, lead, bismuth, and many of the rarer elements.

The comparatively recent work of Morley on the ratio between the atomic weights of oxygen and hydrogen is one of the finest pieces of scientific work in modern times. He has established this ratio by different methods, with an unusual concordance in the results, to be 1 : 15.879.

The work of T. W. Richards on the atomic weights of a large number of the metals should receive special mention. He has improved old methods, devised new ones, and applied them with a skill which is rare. His determinations are to be ranked among the very best which have ever been made.

Table of Atomic Weights. — The most probable atomic weights of the elements, based upon the best determinations, are given in the following table. In preparing this table the tables of Clarke, of Richards, and of the committee of the German Chemical Society have all been carefully considered; also the original determinations themselves, wherever there were appreciable differences between the values chosen by the different authorities. The basis of this table is oxygen = 16.

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[1] *Untersuch. über die Gesetze der chemischen Proportionen.* Leipzig, 1867.

[2] *Lieb. Ann.* **59**, 284, 289 (1846); *Ann. Chim. Phys.* [6], **1**, 303, 321 (1884); *Journ. prakt. Chem.* **74**, 214, 216 (1858).

[3] *Densities of O and H, and the Ratios of their Atomic Weights.* (Smithsonian publication.)

[4] *Amer. Chem. Journ.* **10**, 187; *Ztschr. anorg. Chem.* (1894–1901).

Element	Atomic Weight	Element	Atomic Weight
Aluminium	27.1	Neodymium	143.6
Antimony	120.0	Neon	20.0
Argon	40.0 ?	Nickel	58.7
Arsenic	75.0	Nitrogen	14.04
Barium	137.4	Osmium	191.0
Bismuth	208.3	Oxygen	16.0
Boron	11.0	Palladium	106.5
Bromine	79.95	Phosphorus	31.0
Cadmium	112.35	Platinum	195.0
Cæsium	132.9	Potassium	39.14
Calcium	40.1	Praseodymium	140.45
Carbon	12.0	Rhodium	103.0
Cerium	140.0	Rubidium	85.4
Chlorine	35.45	Ruthenium	101.7
Chromium	52.1	Samarium	150.0
Cobalt	59.0	Scandium	44.0
Columbium	94.0	Selenium	79.2
Copper	63.6	Silicon	28.4
Erbium	166.0	Silver	107.93
Fluorine	19.0	Sodium	23.05
Gallium	70.0	Strontium	87.68
Germanium	72.5	Sulphur	32.06
Glucinum	9.1	Tantalum	183.0
Gold	197.2	Tellurium	127.5
Helium	4.0	Terbium	160.0
Hydrogen	1.01	Thallium	204.1
Indium	114.0	Thorium	233.0
Iodine	126.85	Thulium	170.0 ?
Iridium	193.0	Tin	119.0
Iron	56.0	Titanium	48.15
Krypton	81.8	Tungsten	184.0
Lanthanum	138.5	Uranium	240.0
Lead	206.9	Vanadium	51.4
Lithium	7.03	Xenon	128.0
Magnesium	24.35	Ytterbium	173.0
Manganese	55.0	Yttrium	89.0
Mercury	200.0	Zinc	65.4
Molybdenum	96.0	Zirconium	90.5

RELATIONS BETWEEN ATOMIC WEIGHTS AND PROPERTIES

The Hypothesis of Prout. — It was early noted that if we chose the atomic weight of hydrogen as one, the atomic weights of a large number of elements were either whole numbers or very nearly whole numbers. The slight differences from whole numbers, which were found in several cases, were attributed for the most part to experimental error. Prout observed this relation between the atomic weights, and suggested in 1815 that the explanation of this numerical regularity might be found in the assumption that all the elements are simply condensations of hydrogen. The atoms of the different elements are composed of hydrogen atoms, the number being expressed by the atomic weight of the element. This assumption, which has come to be known as the hypothesis of Prout, was also made some three years later by Meinecke.[1]

The hypothesis of Prout was kindly received, especially by Thomson in England, but was strongly opposed by the great Swedish chemist Berzelius. The latter had devoted much time and labor to the determination of atomic weights, and at this time was the leading authority on such matters. He objected to the method of testing the hypothesis by dropping the fractional part of the atomic weight which had been found experimentally, and of course this point was well taken. Gmelin,[2] on the other hand, was well inclined toward Prout's generalization, and Dumas became a warm supporter of it, after he and Stas had redetermined the atomic weight of carbon and found it to be very nearly 12, in terms of hydrogen as unity.

The element chlorine was, however, very troublesome. The best determinations showed that its atomic weight was 35.5. This led Marignac in 1844 to propose that one-half the atomic weight of hydrogen be taken as the unit. This was the beginning of the downfall of Prout's hypothesis. Having once begun to subdivide the atomic weight of hydrogen to obtain the fundamental unit there was no limit to the process. The next step was taken by Dumas in 1859, when he suggested that one-fourth the atomic weight of hydrogen be taken as the unit, so as to avoid fractions in the more accurately determined atomic weights.

Stas, in 1860, undertook to settle the question as to the correc ness of Prout's original hypothesis. He began that series of atomic weight determinations to which reference has already been made, and which far exceeded in accuracy anything done up to that time. The result is well known. The atomic weights of a number of the elements did not prove to be whole numbers, and the differences from whole numbers were far greater than could reasonably be accounted for on the basis of experimental error. Stas was thus led to abandon the hypothesis, as it was not supported by the facts.

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[1] *Schweigger's Journal*, **22**, 138.

[2] *Handbuch d. theoret. Chemie.*

Attention was again turned to Prout's hypothesis, in 1880, by Mallet.[1] The result of his investigation on the atomic weight of aluminium was to add another element to the list of those which conform to the hypothesis. He took the view that the deviations of the best-known atomic weights from whole numbers may be due to constant errors in the determinations, and pointed out that ten out of eighteen of the best-known atomic weights differed from whole numbers by less than one-tenth of a unit.

While there is then some difference in opinion, even at present,[2] in reference to the real merit of the hypothesis of Prout, there is a strong tendency to reject it as the ultimate expression of the truth. That it is an effort in the right direction is certain, and, indeed, this will be seen when we come to consider, later in this section, the most recent theory of one of the leading physicists of to-day.

The Triads of Döbereiner. — On examining the atomic weights of correlated elements, Döbereiner[3] observed the striking relation, that the atomic weight of the middle member of a group of three such elements was almost exactly the mean between the atomic weights of the first and last members. This will be seen from the following examples: —

	ATOMIC WEIGHT		ATOMIC WEIGHT		ATOMIC WEIGHT
Calcium . .	40.1	Chlorine . .	35.4	Sulphur . .	32.1
Strontium . .	87.7	Bromine . .	80.0	Selenium . .	79.2
Barium . . .	137.4	Iodine . . .	126.8	Tellurium .	127.5

The atomic weight of strontium is close to the mean of calcium and barium (88.7); that of bromine is not widely different from the mean of chlorine and iodine (81.1); while the atomic weight of selenium is very close to the mean of sulphur and tellurium (79.8). These correlated groups of three elements came to be known as triads, and from their discoverer as Döbereiner triads.

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[1] *Amer. Chem. Journ.* **3**, 95 (1881).

[2] Strutt: *Phil. Mag.* [6], **1**, 311 (1901).

[3] *Pogg. Ann.* **15**, 301 (1825).

The Work of Cannizzaro and of De Chancourtois. — It was impossible that any comprehensive generalization should be reached connecting atomic weights with any property, until some uniform system of atomic weights had been adopted. Confusion was reduced to order in this line by Cannizzaro. He considered Avogadro's law as the basis of atomic weight determinations, and gave us the conception of atom which still prevails. With these comparable atomic weights chemists could now deal, and relations between those weights and properties of the elements, which have proved to be of the greatest service in the development of inorganic chemistry, were soon pointed out. It is thought by some that De Chancourtois was the first to call attention to relations which can fairly be regarded as the logical precursors of the periodic law. He suggested[1] that the atomic weights be arranged in a particular way in the form of a screw, and showed that relations existed between the positions of the elements and their properties. In an obscure way he seems to have hinted at the fundamental idea underlying the later discovery, that the properties depend upon the atomic weights, but certainly this was neither clearly conceived nor tersely expressed.

The Octaves of Newlands. — The question of relations between the atomic weights was taken up by Newlands shortly after the work of De Chancourtois. In his earlier papers[2] he pointed out connections between atomic weights and chemical properties, but it was not until 1864 that he announced any important discovery. In a brief note to the *Chemical News*,[3] "On Relations among the Equivalents," he arranged the elements in the order of their equivalents and stated that "it will be observed that elements having consecutive numbers frequently either belong to the same group or occupy similar positions in different groups. . . . The difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from given one is a kind of repetition of the first, like the eighth note an octave in music." In the following year Newlands announce his "Law of Octaves" in a very brief note:[4] "If the elements a arranged in the order of their equivalents with a few slight transpositions, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will be seen that the members of analogous elements generally differ either by 7, or by some multiple of 7. In other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." The table given by Newlands brings out the relation to which he refers. It is of such historical interest that it should be given in this connection.

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[1] *Vis Tellurique, Classement naturel des Corps Simples*, etc. Paris, 1863.

[2] *Chem. News*, **7**, 70 (1863); **10**, 11, 59 (1864).

[3] *Ibid.* **10**, 94 (1864).

[4] *Ibid.* **12**, 83 (1865).

NEWLANDS' TABLE

H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
G	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba & V	45	Pb	54
Bo	4	Al	11	Cr	19	Y	24	Ce & La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Os	51

A comparison of this table with the periodic system proper will show that it contains more than the germ of this important generalization.

The Periodic System of Mendeléeff and Lothar Meyer. — The periodic system of the elements, as we now have it, was undoubtedly discovered independently, and very nearly simultaneously, by the Russian, Mendeléeff, and the German, Lothar Meyer. The latter published in 1864[1] a table containing most of the then known elements, arranged in the order of their atomic weights. In this arrangement elements which are closely allied in their chemical properties appear in the same columns, but the system is so incomplete that it is scarcely an advance on that of Newlands.

The first to point out the most important features in the arrangement of the elements according to their atomic weights was undoubtedly Mendeléeff. In 1869[2] he arranged the elements in a table in the order of their atomic weights, and showed clearly that there is a periodic recurrence of properties as the atomic weights increase. This will be seen best in the following table:[3] —

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[1] *Die modernen Theorien der Chemie.*

[2] *Journ. Russ. Chem. Soc.* 60 (1869).

[3] *Lieb. Ann. Suppl.* **8**, 133 (1874).

MENDELÉEFF'S ORIGINAL TABLE

Series	GROUP I — R_2O	GROUP II — RO	GROUP III — R_2O_3	GROUP IV RH_4 RO_2	GROUP V RH_3 R_2O_5	GROUP VI RH_2 RO_3	GROUP VII RH R_2O_7	GROUP VIII — RO_4
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	Y=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	Di=138	Ce=140	—	—	—	— —
9	(—)	—	—	—	—	—	—	— —
10	—	—	Er=178	La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	— —
12	—	—	—	Th=231	—	U=240	—	— —

This table contains all the elements known at that time, and the blank spaces indicate that the elements which would naturally fall into these places were unknown. The general plan of the Mendeléeff table is simple. All the elements are arranged in succession in the order of their increasing atomic weights. If we start with the element with the smallest atomic weight next to hydrogen, *i.e.* lithium, and arrange the succeeding elements in the order of their atomic weights up to fluorine, we find that the next element, sodium, has properties quite similar to those of lithium. If we place sodium in the same vertical column with lithium, and then arrange the next elements in the order of their atomic weights, we find that magnesium falls in the same column with beryllium, aluminium with boron, silicon with carbon, phosphorus with nitrogen, sulphur with oxygen, and chlorine with fluorine. This is, of course, a remarkable relation, since in every case those elements which fall in the same vertical column resemble each other very closely. The first seven elements, starting (not with hydrogen, since it does not fit into this scheme) with lithium, and ending with fluorine, agree very closely in propert with the second set of seven elements arranged as in the above tab We come now to the first member of the next series of seven ments, — potassium; it falls right into the group with lithium and sodium, calcium with beryllium and magnesium, titanium with carbon and silicon, vanadium with nitrogen and phosphorus, chromium with oxygen and sulphur, and manganese with fluorine and chlorine. Here again striking analogies appear between the different members in the same groups. The blank space between calcium and titanium contained no known element when this table was prepared. The element has since been discovered, and has peculiar interest in connection with this whole system; to this reference will again be made. After we leave manganese we encounter one of the weakest points of the Periodic Law. The next elements in order of atomic weights are iron, cobalt, and nickel; but it is obvious that neither of these can be placed in the same group with the alkali metals. They must therefore be set aside and left out of the system. Then we come to copper, which is very questionably placed with the members of group I. Then irregularities appear again. At the end of the sixth series we find three or four more elements which do not fit into the scheme, but after leaving these, regularities again begin to manifest themselves.

A more detailed account of the relations between properties and atomic weights will be taken up a little later. The above suffices to show the general relation, and also the periodic recurrence of properties with increase in the atomic weights.

The same general relations as those pointed out by Mendeléeff were undoubtedly discovered independently by Lothar Meyer,[1] and published the following year (1870). His table is almost exactly the same as that of Mendeléeff, and he recognized clearly the periodic recurrence of properties. To quote his own words,[2] "We see from the table that the properties of the elements are, for the most part, *periodic* functions of the atomic weights."

Meyer has since changed the form of this table, arranging it as a spiral. "If we regard this table as wrapped around an upright cylinder so that the right and left sides touch; therefore, nickel next to copper, palladium to silver, and platinum to gold, we obtain, as is easily seen, a continuous series of all the elements in the order of their atomic weights, arranged in the form of a spiral. The elements which, in this arrangement, fall into the same vertical column, form a natural family, the members of which, however, bear a very unequal resemblance to one another." This spiral arrangement of the elements is shown in the following table: —

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[1] *Lieb. Ann. Suppl.* 7, 354 (1870).

[2] *Ibid.*, p. 358.

Meyer's Table (using the present atomic weights)

I	II	III	IV	V	VI	VII	VIII		
Li 7.03	Be 9.1	B 11.0	C 12.0	N 14.04	O 16.0	F 19.0			
Na 23.05	Mg 24.35	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45			
K 39.14	Ca 40.1	Sc 44.0	Ti 48.15	V 51.4	Cr 52.1	Mn 55.0	Fe 56.0	Co 59.0	N 58
Cu 63.6	Zn 65.4	Ga 70.0	Ge 72.5	As 75.0	Se 79.2	Br 79.95			
Rb 85.4	Sr 87.68	Y 89.0	Zr 90.5	Nb 93.7	Mo 96.0		Ru 101.7	Rh 103.0	P 10
Ag 107.93	Cd 112.35	In 114.0	Sn 119.0	Sb 120.0	Te 127.5	I 126.85			
Cs 132.9	Ba 137.4	La 138.5	Ce 140.0						
		Yb 173.0		Ta 183	W 184.0		Os 191.1	Ir 193.0	P 19
Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208.3					
			Th 233.0		U 240.0				

This table brings out more clearly than that of Mendeléeff idea of a continuous arrangement of all the elements in the orde their atomic weights. And it is equally successful in showing periodic nature of the properties of the elements. The blank spa are for unknown elements. Meyer calculated the probable ato weights of these elements, but these values being for the most p unverified, are omitted.

Chemical Properties and Atomic Weights. Combining Power

If we start with lithium in Mendeléeff's table and proceed to right along the second series, this striking fact is observed: elements increase in their power to combine with oxygen regula from left to right. Take first the power of the elements to comb with oxygen. Lithium forms the compound Li_2O, beryllium BeO, aluminium Al_2O_3, carbon CO_2, nitrogen N_2O_5; oxygen and fluorine may be disregarded for the moment. Take the third series. Sodium forms the compound Na_2O, magnesium MgO, aluminium Al_2O_3, silicon SiO_2, phosphorus P_2O_5, sulphur SO_3, and chlorine Cl_2O_7. The fourth and fifth series show the same regularities, and similar relations are observed throughout the table. The best example of an element octavalent toward oxygen is osmium, which forms the compound OsO_4. We have, then, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4.

We may say in general that the power of the elements to combine with oxygen is smallest in group I, and increases regularly by unity in each succeeding group; reaching a maximum in group VIII, where, at least in the case of osmium, it is eight.

Results of a similar character are obtained if we study the power of the elements to combine with chlorine. Sodium combines with one chlorine atom, magnesium with two, aluminium with three, silicon with four, phosphorus with five. Sulphur does not combine directly with six chlorine atoms, but combines with both oxygen and chlorine, forming the compound SO_2Cl_2, in which the sulphur has a valence of four towards the oxygen, and of two towards the chlorine, or of six in all. But there is a member of group VI which combines directly with six chlorine atoms. This is tungsten, in the tenth series. We would express the combining power of the elements toward chlorine as follows: —

$$\begin{array}{llllll} NaCl, & MgCl_2, & AlCl_3, & SiCl_4, & PCl_5, & SO_2Cl_2. \\ & & & & & (WCl_6) \end{array}$$

Exactly the same regularity which was observed in the case of oxygen exists here. The elements in group I have the smallest power of combining with chlorine, and this increases by unity from group to group as we pass from left to right; reaching a maximum of six in the sixth group. We know of no element which has the power of combining directly with more than six atoms of chlorine.

When we examine the power of the elements to combine with hydrogen, a regularity is observed, but of a different kind from those already considered. The elements in groups I, II, and III in general do not combine directly with hydrogen to form stable compounds, although hydrides of some of these elements are known. When we come to group IV, we find in carbon a remarkable power to combine with hydrogen. The highest valence of the elements toward hydrogen is manifested in this group, where one atom of the element combines directly with four atoms of hydrogen. As we pass to the right the power of the elements to combine with hydrogen decreases, and decreases regularly. Nitrogen combines with three atoms of hydrogen, oxygen with two, and fluorine with one. Starting with group IV, we have: —

$$CH_4,\quad NH_3,\quad OH_2,\quad FH.$$

The valence toward hydrogen manifests itself to a maximum degree in group IV, and diminishes regularly as the valence toward oxygen increases.

The relations pointed out between the combining power of the elements are general, extending throughout the entire table of the elements. It should, however, be stated here that there are many breaks in the system, irregularities appearing on every hand. Some of these defects will be pointed out in a later paragraph.

Relations within the Groups

In the table of Mendeléeff the members of the even series are placed above one another, and, similarly, the members of the odd series. Each group is thus divided into two columns, whose meaning at first sight is not so apparent. If the members of these two columns in any group be compared, it will be found that those elements which fall in the same column are more closely allied in their general properties than the elements in different columns in the same group. Thus, lithium, potassium, rubidium, and cæsium resemble each other chemically more closely than they resemble sodium, copper, silver, and gold. This is more strikingly shown by the second group, where beryllium, calcium, strontium, and barium fall in one column, and magnesium, zinc, cadmium, and mercury in the other. The chemical relation between the individuals in a given column is very close in this group, while it is not so striking between the members of the different columns. Thus, calcium is much more closely related to strontium and barium than it is to zinc or mercury; and, similarly, cadmium is much more closely allied to zinc and mercury than it is to the calcium group.

Passing to the last group, chlorine, bromine, and iodine fall in the same column, and are very similar in their chemical behavior, while their relation to manganese is at first sight not very close. These facts, while purely empirical, are of profound interest, and give to the Periodic Law a deep significance. It is certainly true that the members of even series are more closely related to one another than they are to members of odd series, and the same obtains for the relations between the odd series. We seem to have here not only a Periodic System of the elements, but one such system within another.

Basic and Acid Properties

At least one other relation between the chemical properties of the elements and their atomic weights must be pointed out. In any given series the element with the lowest atomic weight has the smallest power to combine with oxygen, as has already been stated. It has also the strongest basic character. Thus, lithium is more basic than beryllium, which, in turn, is far more basic than boron. Sodium is more basic than magnesium, while aluminium begins to show acid properties in its hydroxide. Potassium is far more basic than calcium, rubidium than strontium, cæsium than barium. The difference between copper and zinc, and silver and cadmium, is not so striking. As we find the most basic elements in the first group, we would expect to find the most acid in the last, and such is the case. Through the middle groups we find elements which show, now more, now less basic or acid properties, depending upon conditions; but in the last column of the last well-defined group we have elements which manifest only acid-forming properties. The hydrogen and hydroxyl compounds of the halogens are always acids, and always react as such with all other substances. These facts are very surprising. As we pass upward in the table of atomic weights, say from oxygen, the first element we encounter is fluorine, with very pronounced acid-forming properties. The element with the next higher atomic weight is sodium, which is one of the strongest base-forming elements. Similarly, next to sulphur comes chlorine, which has much stronger acid-forming properties than sulphur, but next to chlorine comes potassium, which is one of the most strongly basic elements. In the same way bromine is followed by rubidium, and iodine by cæsium, where the contrast in properties is quite as great as in the cases referred to above.

Many other relations[1] between chemical properties and atomic weights have been pointed out, but those already considered are among the most important.

Physical Properties and Atomic Weights. — The relations between many of the physical properties of the elements and their atomic weights are striking. A number of these have been pointed out by Lothar Meyer.[1]

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[1] *Lieb. Ann. Suppl.* 8, 133–229 (1872). Mendeléeff, *Principles of Chemistry*, II.

Atomic Volumes. — The atomic volume of an element is the atomic weight divided by the specific gravity or density of the element in the solid form. In this connection the atomic weight of hydrogen is taken as the unit, and the specific gravity of water as the unit of density. Take the first element in the periodic system which exists normally in the solid state, — lithium. Its atomic weight is 7, its density 0.59. The atomic volume of lithium $= \frac{7}{0.59} = 11.9$.

Meyer[2] plotted the curve showing the change in the atomic volume with increase in atomic weight, and found that it had remarkable properties. The curve is shown in Fig. 1. The abscissas are atomic weights, and the ordinates atomic volumes.

In some cases the specific gravity of the element in the solid form could not be determined; as with hydrogen, oxygen, nitrogen, fluorine, etc. In the places corresponding to these elements the curve is a dotted line.

We see at once from the curve that the atomic volume is a periodic function of the atomic weight. As the atomic weight increases, the atomic volume decreases and increases regularly. The curve presents five maxima, at which we find the five alkali metals, — lithium, sodium, potassium, rubidium, and cæsium. At the minima fall those elements whose atomic weights are approximately the mean between the atomic weights of the element at the preceding and succeeding maxima. In fact, at the third, fourth, and fifth minima we find the elements which do not fit into Mendeléeff's table, and are placed by themselves in group VIII. We see also in this curve the distinction between the short and long periods of Mendeléeff's table. The first loop of the curve contains the first short period, or the elements from lithium to fluorine; the double loop from sodium to nickel the first long period, and so on. It sometimes occurs that elements with similar chemical properties have very nearly the same atomic volumes, as with chlorine, bromine, and iodine.

It is quite remarkable that for elements with very nearly the same atomic volumes, the properties are markedly different, depending upon whether the element is on an ascending or a descending arm of the curve; and, therefore, upon whether the element with the next higher atomic weight has a larger or smaller atomic volume than its

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[1] *Die modernen Theorien der Chemie.*

[2] *Lieb. Ann. Suppl.* 7, 354 (1870).

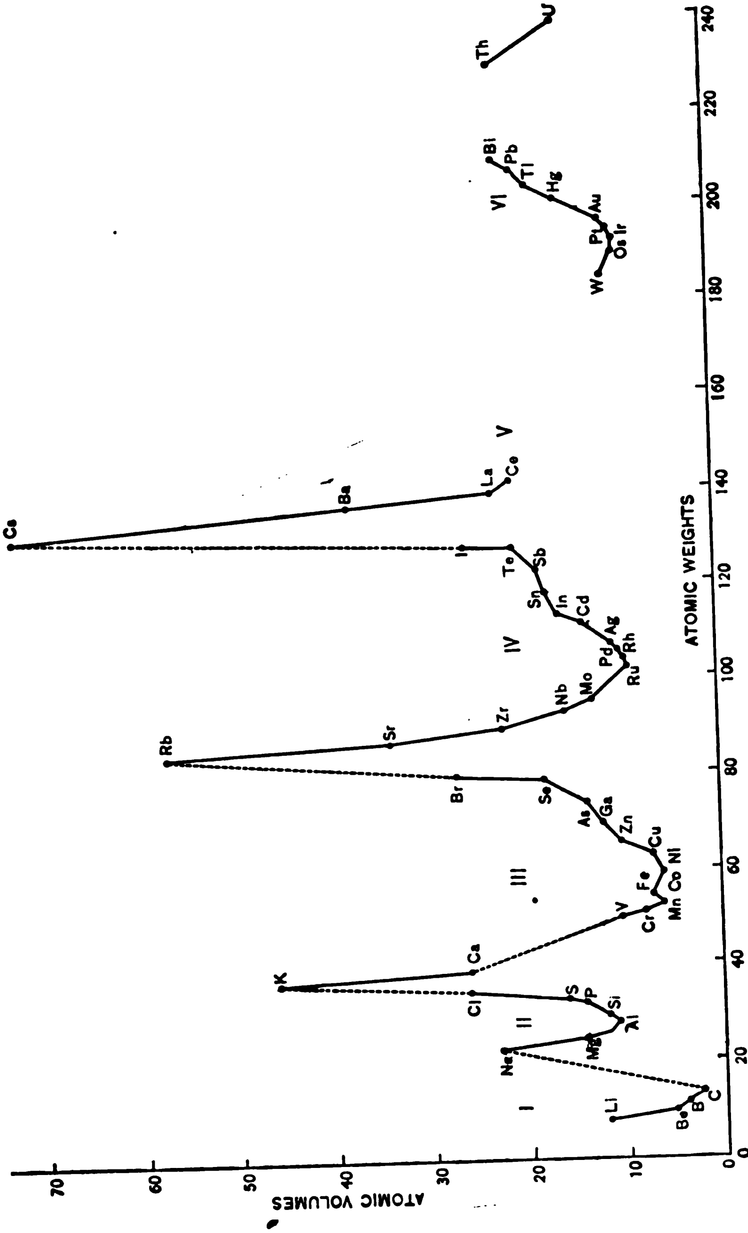
ATOMIC VOLUMES
70
60
50
40
30
20
10
0
ATOMIC WEIGHTS
0
20
40
60
80
100
120
140
160
180
200
220
240
I
II
III
IV
V
VI
Li
Be
B
C
Na
Mg
Al
Si
P
S
Cl
K
Ca
Cr
V
Mn
Fe
Co
Ni
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

FIG. 1.

own; *e.g.* phosphorus and magnesium, chlorine and calcium. If we follow the curve from its origin, we find the most strongly base-forming elements at the maxima, and the remainder on the descending arms of the curve. The acid-forming elements are on the ascending arms of the curve. Relations between a number of physical properties [redacted] re-

rate at which metals dissolve and diffuse in mercury by

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[1] Meyer: *Die modernen Theorien der Chemie.*

[2] *Die modernen Theorien der Chemie.*

[3] *Journ. Chem. Soc.* 69, 1679 (1896).

placing a piece of the metal on the top of a column of mercury in a glass tube. The metals chosen were those which would amalgamate most easily. These, as will be seen, belong to the uneven series in Mendeléeff's table. For metals in the same group the rate of solution and diffusion increases with increase in atomic weight. Copper dissolves and diffuses less rapidly than silver, and silver less than gold. The order in group II is Mg, Zn, Cd, Hg; in group III, Al, In, Tl; in group IV, Sn, Pb; in group V, As, Sb, Bi. In the different series the solution and diffusion are greater the nearer the metal stands to mercury. The metals of the mercury group, in general, diffuse most rapidly. The farther the element is removed from mercury, the less the solution and diffusion. These relations are clearly shown in the following table. The arrows point in the direction of increase in solubility and diffusion.

SERIES	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V
3		Mg ↓	Al ↓		
5	Cu → ↓	Zn ↓			← As ↓
7	Ag → ↓	Cd ↓	← In ↓	← Sn ↓	← Sb ↓
11	Au →	Hg ↓	← Tl	← Pb	← Bi

Old Atomic Weights corrected and New Elements predicted by Means of the Periodic System. — A scientific theory to be of the highest value must not simply be able to account for all the facts known, but must suggest new possibilities which were not realized when the theory was first announced. The Periodic Law has fulfilled the latter condition in a beautiful way. By means of it a number of erroneous atomic weights were corrected. The atomic weight of indium was supposed to be 75.6, and the composition of the oxide, InO. This would place it in the Periodic System between arsenic and selenium. The chemical properties and atomic volume showed that it belonged rather between cadmium and tin. Meyer[1] gave it the atomic weight 113.4 ($75.6 \times 1\frac{1}{2}$), and regarded the oxide as having the composition In_2O_3. This was confirmed by Bunsen[2] from specific heat determinations. The atomic weight of beryllium was thought to be 4.54, or $4.54 \times 2 = 9.08$, or $4.54 \times 3 = 13.62$. The chemical and physical nature of the element showed that it must come between lithium and boron, and, indeed, be the head of the magnesium-calcium group. The true atomic weight was subsequently shown to be 9.08. Similarly, uranium was supposed to have the atomic weight 60, 120, or 180, and it was difficult to decide between these values. But it was more probably 240 in terms of the Periodic System; and this conjecture has also been verified. It should be observed that in these cases the vapor-density method of determining the number of atoms in the molecule could not be employed.

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[1] *Lieb. Ann. Suppl.* **7**, 362 (1870).

[2] *Pogg. Ann.* **141**, 1 (1870).

The Periodic System has been used not simply to decide between an atomic weight and a multiple of this quantity, but to actually correct atomic weights imperfectly determined. Bunsen found the atomic weight of cæsium to be 123.4. This value was smaller than would be expected from the Periodic System. The correct atomic weight of cæsium was found later[1] to be 132.7, which is in perfect accord with the system. More recent work in connection with osmium, iridium, platinum, and gold make it very probable that the order for these four elements suggested by the system is the correct one, and that the earlier determinations of atomic weights contain considerable error.

The prediction of the existence of unknown elements and the nature of their properties has been so beautifully verified in a number of cases that this has become the most striking application of the Periodic Law. Mendeléeff[2] recognized that the atomic weight and other properties of an element can be determined from the properties of the two neighboring elements in the same series and the two neighboring elements in the same half of the same group. The properties are as a rule the mean of those of the four elements. These four elements were termed by Mendeléeff the *Atomic Analogues* of the element in question. This will be clear from the following example: —

	Ca 40	
Rb 85	Sr 87	Yt 88
	Ba 137	

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[1] Bunsen: *Pogg. Ann.* **119**, 1 (1863).

[2] *Lieb. Ann. Suppl.* **8**, 165 (1872).

The atomic weight of strontium is the mean of the atomic weights of its four analogues, and the same holds in general for the other properties.

On the basis of this fact Mendeléeff[1] predicted the existence and properties of a number of elements which had not been discovered when the Periodic Law was announced. The element predicted was named from the element in the same group which immediately precedes it, adding the prefix "eka." In the third group the element immediately following boron was unknown, and was termed *ekaboron*. Since it followed calcium with an atomic weight of 40, and preceded titanium whose atomic weight is 48, its atomic weight must be 44. The oxide must have the composition Eb_2O_3 and have the same relation to aluminium oxide as calcium oxide does to magnesium oxide. The sulphate must be less soluble than aluminium sulphate, just as calcium sulphate is less soluble than magnesium sulphate. The carbonate would be insoluble in water. The salts would be colorless and form gelatinous precipitates with potassium hydroxide and carbonate, and disodium phosphate. The sulphate would yield a double salt with potassium sulphate. Few of the salts would be well crystallized. The chloride would probably be less volatile than aluminium chloride, since titanium chloride boils higher than silicon chloride, and calcium chloride is less volatile than magnesium chloride. The chloride would be a solid, its volume about 78, and its density about 2. The specific gravity of the oxide would be about 3.5, and its volume about 39. Ekaboron would be a light, non-volatile, difficultly fusible metal, which will decompose water only on warming; would dissolve in acids with evolution of hydrogen, and would have a specific gravity of about 3.

In a similar manner Mendeléeff predicted the existence and properties of an element between aluminium and indium, terming it *ekaaluminium*. The atomic weight would be approximately 68.

Again, an element should exist between silicon and tin, and this was termed *ekasilicium*, with an atomic weight of 72.

The properties of the last two elements and their compounds are described in considerable detail from the properties of their atomic analogues, but for these the original paper[2] must be consulted.

These elements have now all been discovered. The element described by Nilson[3] as scandium, proved to be ekaboron, having an atomic weight of 44. Gallium, discovered by Lecoq de Boisbaudran,[1] was the predicted ekaaluminium, with an atomic weight of 70. And germanium, discovered by Winkler,[2] proved to be the ekasilicon, having an atomic weight of 72. The properties of these elements and their compounds corresponded about as closely with the properties predicted for them as the atomic weights.

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[1] *Lieb. Ann. Suppl.* **8**, 196 (1872).

[2] *Loc. cit.*

[3] *Ber. d. chem. Gesell.* **12**, 554 (1879).

Imperfections in the Periodic System. — While admiring the many deep-seated relations which are brought out by the Periodic System, we must not fail to observe that it is far from complete. At the very outset there is evidence of this incompleteness — hydrogen does not fit at all into the scheme, and yet it is one of the most important elements. In the very first group of the elements, again, there is apparent inconsistency. Along with lithium, potassium, rubidium, and cæsium, we find copper, silver, and gold. There is evidently no very close connection between the last three elements and the first four. Further, sodium does not fall into the same division of the group with the other strongly alkaline metals, but with copper, silver, and gold. It is at once apparent that sodium is not as closely allied to these elements as to the alkali metals which constitute the other division of group I.

Passing over the intermediate groups, which contain a number of more or less serious inconsistencies, we find in group VII manganese placed with the halogens and not falling into the same group either with chromium or with iron. The relations of manganese to the halogens are not more striking than the differences, and we do not find manganese falling into the same division of the group with chlorine, bromine, and iodine, but with fluorine, to which it bears a much less close resemblance than to the remaining halogens.

When we come to group VIII, we find nothing but discrepancies. These elements do not fit into the system at all, and are placed by themselves as a separate group. It is questionable whether it is desirable to call this group VIII, since it is in no chemical or physical sense a true extension of the system one step beyond group VII. Take as an example the power of the elements to combine with oxygen. There is a regular increase in this power from unity in group I, through the several groups up to group VII, — where we find the compounds Cl_2O_7, Br_2O_7, I_2O_7, — fluorine not combining at all with oxygen. Of all the elements in the so-called group VIII, there is only one, osmium, which has a valence of eight towards oxygen. The remainder all show a lower valence towards this element.

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[1] *Compt. rend.* **81**, 493, 1100; **82**, 168, 1036, 1098; **83**, 611, 636, 663, 824, 1044; **86**, 941, 1240 (1875–1878).

[2] *Ber. d. chem. Gesell.* **19**, 210 (1886); *Journ. prakt. Chem.* [2], **34**, 177 (1886); **36**, 177 (1887).

It seems better to recognize these elements as distinct exceptions, which do not fit into the Periodic System at all satisfactorily; yet even here we must recognize a certain periodicity in the recurrence of these exceptions, and that they occur in every case in groups of three. The Periodic System seemed to be hard pressed for a time to find a place for some of the elements described by Ramsay as occurring in the atmospheric air. Quite recently, however, Ramsay has shown that these elements have a place in the Periodic System. These apparent discrepancies in the Periodic System have not been pointed out with the desire to undervalue the merits of this important generalization, but simply to arrest attention to the fact that the system is still far from complete. What has already been accomplished is of tremendous importance, as is shown by the single fact that we can correct atomic weights and predict the properties of elements entirely unknown. Indeed, we can do more; we can predict with what elements the unknown element in question would form compounds, the composition of these compounds, and even the color and other physical properties possessed by them.

We shall probably never have a complete and perfect Periodic System of the elements until our knowledge of these substances and their compounds is far deeper than at present. If the system was perfect and complete, it is more than probable that it would lose some of the interest which it now possesses; since it would then offer far less incentive to investigation, which is one of the best tests of the scientific value of any theory or generalization.

Thomson's Theory of the Relation between the Elements. — The hypothesis of Prout that the atoms of the different elements are aggregations of hydrogen atoms was shown at the beginning of this section to be untenable. J. J. Thomson,[1] from a study of the passage of cathode rays through gases, has recently been led to a theory as to the composition of the atoms of elementary substances, which in a way is analogous to the hypothesis of Prout, but which differs very materially from it. Says Thomson,[2] "As the cathode rays carry a charge of negative electricity, are deflected by an electrostatic force as if they were negatively electrified, and are acted on by a magnetic force in just the way in which this force would act on a negatively electrified body moving along the path of these rays, I can see no escape from the conclusion that they are charges of negative electricity carried by particles of matter. The question next arises, What are these particles? are they atoms, or molecules, or matter in a still finer state of subdivision? To throw some light on this point, I have made a series of measurements of the ratio of the mass of these particles to the charge carried by it."

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[1] *Phil. Mag.* **44**, 293 (1897).

[2] *Ibid.*, p. 302.

If we represent the mass of each of the particles by m, and the charge carried by the particles by e, two important facts were discovered in connection with the values of $\frac{m}{e}$.

1st. The value of $\frac{m}{e}$ is independent of the nature of the gas.

2d. It is very small (10^{-7}) as compared with the smallest value of this quantity previously known, 10^{-4}, which is the value of the hydrogen ion in electrolysis. It is, therefore, very probable that the carrier is the same in the different gases, and since e is the same as in electrolysis, m must be very much smaller than ordinary molecules.

To again quote from Thomson's paper[1]: "The explanation which seems to me to account in the most simple and straightforward manner for the facts is founded on a view of the constitution of the chemical elements which has been favorably entertained by many chemists; this view is that the atoms of the different chemical elements are different aggregations of atoms of the same kind. In the form in which this hypothesis was enunciated by Prout, the atoms of the different elements were hydrogen atoms; in this precise form the hypothesis is not tenable, but if we substitute for hydrogen some unknown primordial substance, X, there is nothing known which is inconsistent with this hypothesis. . . .· Thus, on this view we have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state; a state in which all matter — that is, matter derived from different sources such as hydrogen, oxygen, etc. — is of one and the same kind; this matter being the substance from which all the chemical elements are built up."

These very small particles, or primordial atoms into which the molecules of the gas are dissociated, have been termed by Thomson, "corpuscles." These are evidently much smaller than the molecules of the gas, and would give a constant value for $\frac{m}{e}$, independent of the nature of the gas, for the "corpuscles" are the same whatever the gas might be.

We have thus traced in this section the theories as to the relations between the atoms of the different elements. Also the relations between the relative weights of the atoms of elementary substances, and the chemical and physical properties of those substances. The question has not thus far been raised as to the actual nature of the atom, or as to its absolute size or weight. To such problems we will now turn.

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[1] *Loc. cit.*, p. 311.

THE NATURE OF ATOMS AND THE SIZE OF MOLECULES

The Theory of Vortex Atoms. — A paper on "Vortex Atoms" was presented by Lord Kelvin to the Royal Society of Edinburgh in 1867.[1] He had been attracted by Helmholtz's discovery of the law of vortex motion in a perfect fluid, which appeared to him to contain a rational explanation of the nature of the atom itself.[2] "This discovery inevitably suggests the idea that Helmholtz's rings are the only true atoms. For the only pretext seeming to justify the monstrous assumption of infinitely strong and infinitely rigid pieces of matter, the existence of which is asserted as a probable hypothesis by some of the greatest modern chemists in their rashly worded introductory statements, is that urged by Lucretius and adopted by Newton; that it seems necessary to account for the unalterable distinguishing qualities of different kinds of matter. But Helmholtz has proved an absolutely unalterable quality in the motion of any portion of a perfect liquid, in which the peculiar motion which he calls 'vortex motion' has once been created. Thus, any portion of a perfect liquid which has 'vortex motion' has one recommendation of Lucretius' atom, — infinitely perennial specific quality. To generate or to destroy 'vortex motion' in a perfect fluid can only be an act of creative power."

Maxwell[3] discusses the vortex theory of Kelvin in some detail, and points out that the fluid must be a material substance with continuous motion, and the mass of any moving portion must remain constant. In addition, it must be incompressible, homogeneous, and continuous. If from every point of a closed curve vortex lines are drawn in both directions, the tubular surface thus formed is the so-called vortex tube. The strength of the tube is the product of the area of any section of the tube and the mean velocity of rotation. Maxwell shows that the following facts obtain for such a finite vortex tube in an infinite fluid: It so returns into itself as to form a closed ring, whence the term "vortex ring." It always consists of the same portion of the fluid, and therefore has an invariable volume. The strength remains invariable. A portion of the fluid once in rotational motion must forever continue so to move, and all portions not originally in such motion can never enter into it. A vortex tube can never pass through any other such tube, or through any of its own convolutions.

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[1] *Proc. Roy. Soc.*, Edinb., 1867, p. 94.

[2] *Ibid.*, p. 94.

[3] *Encyclopædia Britannica*, article "Atom."

Maxwell thinks "that the vortex ring theory of the atom satisfies more of the necessary conditions than any other theory of the atom thus far suggested."

Applications of the Theory to Chemical Phenomena. — The application of the theory of the vortex atom to chemical phenomena we owe chiefly to J. J. Thomson.[1] The simplest atom consists of a single vortex ring; the more complex atoms of two or more of these rings linked together. The single rings may differ in volume, which would account for the difference in properties observed. Chemical action consists in the union of the vortex rings. If the rings are of the same kind, we have atoms of elementary substances uniting to form molecules. If the rings are of different kinds, we have the two elements of which these rings are the atoms uniting chemically. If two vortex rings united as above described are brought into the presence of other vortex rings, they will separate, since their velocities of translation will become different, their radii being changed by different amounts.

Atoms of all the elementary substances are then to be regarded as made up of vortex rings. Some consist of only one ring, others of two rings linked together, others of three, and so on up to six vortex rings. It is shown that no atom can consist of more than six of these rings arranged symmetrically, and this is of chemical importance, as we shall see. One atom of an elementary substance may unite with another of the same kind, forming a molecule consisting of two atoms, as we believe to be the case in hydrogen, chlorine, oxygen, etc. Three or four elementary atoms might unite and form a molecule, but, as Thomson points out, there is much less chance of their combining in this way than in pairs.

Each vortex ring in the atom corresponds to one bond or unit valence, and the number of vortex rings contained in the atom determines its valency or combining power.

The conclusion that if these rings are linked in the most symmetrical manner the largest possible number contained in any atom is six, can be tested by chemical means. If the maximum number of rings in an atom is six, and each ring corresponds to one valence or combining power, then the maximum number of the simplest single-ring atoms with which any atom could combine, is six. There is no case known in the whole field of chemistry where one atom of any substance combines with more than six atoms of any other substance. And further, there is at least one compound known (WCl_6) where an atom of one element does combine with six atoms of another element. This agreement between theory and fact is so striking that it cannot be regarded as an accidental coincidence.

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[1] *Motion of Vortex Rings*, pp. 109–124.

The theory of vortex atoms is also wonderfully in accord with some of the facts discovered by a spectroscopic examination of the elements.

What the ultimate fate of the theory of "vortex atoms" will be, it is impossible to say. The enormous difficulties involved in testing any theory as to the nature of the atom itself are apparent to any one. All that can be stated at present is that this is by far the best theory that we have as to the nature of the atom, and that it accords with many important facts both in chemistry and in physics.

The Size of Molecules. — This chapter on atoms and molecules should not be closed without a brief reference to Kelvin's calculation of the approximate size of molecules. He[1] calls attention to the fact that atoms cannot be infinitesimally small, since if they were, chemical reactions would have to take place with infinite velocity. Recognizing that atoms have finite size, he obtained data from several sources, and especially from the study of the electrical relations between copper and zinc, and also from the study of the thickness of the soap-bubble, for calculating the size of molecules. The results obtained by some four different methods were of the same order of magnitude. If two millions of molecules were arranged side by side, the row would be a millimetre in length, and two hundred million, million, million of hydrogen molecules would weigh a milligram. The number of molecules in a cubic centimetre of gas under normal conditions cannot be greater than 6×10^{21}, or six thousand, million, million, million. Since the densities of liquids and solids are from five hundred to sixteen thousand times that of the air, the number of molecules in a cubic centimetre of the liquid or solid must be from 3×10^{24} to 3×10^{26}.

Numbers of such magnitude are entirely incomprehensible, and in order to form any conception of them, we must translate them into terms with which the mind can deal. This has already been done for us by Lord Kelvin in the last paragraph of his paper:[2] —

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[1] *Nature*, March 31st, 1870. Reprinted in *Amer. Journ. Science* [2], **50**, 38 (1871). Also *Lieb. Ann.* **157**, 54 (1871).

[2] *Loc. cit.*

"To form some conception of the degree of coarse-grainedness indicated by this conclusion, imagine a raindrop, or a globe of glass as large as a pea, to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be coarser-grained than a heap of small shot, but probably less coarse-grained than a heap of cricket balls."

Perhaps the best demonstration of the almost unlimited divisibility of matter is furnished by some of the aniline dyes or by fluoresceïn, where one part is capable of coloring or rendering fluorescent at least one hundred million parts of water.

The absolute size of the molecules has been calculated on entirely different grounds by Nernst, J. J. Thomson, and others. The results obtained are, in general, of the same order of magnitude, and in many cases agree as closely as we could expect when we consider the enormous difficulties involved in such calculations.

CHAPTER II

GASES

LAWS OF GAS-PRESSURE

Properties of Gases. — We know matter in three states of aggregation: gas, liquid, and solid. These differ from one another in many respects; but the most striking difference is in the relative ease with which the particles can move among one another. In a gas there is comparatively little resistance offered to the movements of the molecules; the friction of one particle against another is comparatively small. In a liquid there is much greater resistance offered to the movement of the parts, the inner friction being many times greater than in a gas; while in a solid the parts are relatively fixed, and movement is accomplished only by subjecting the solid to very great pressures.

Another striking difference between gases, and liquids and solids, probably due to the same cause, is the almost unlimited power of expansion possessed by the former. A gas expands and fills the entire space placed at its disposal. A liquid takes the form of the containing vessel on all sides except above, but has its own definite volume for a definite temperature, and this varies but little for large changes in pressure. A solid has its own definite shape and volume, independent of the shape and size of the containing vessel. This volume varies with the temperature according to definite laws, and is only slightly changed by change in pressure. Gases differ from liquids and solids also in that they represent matter in a very dilute form. A little matter is distributed through a large space, or as it is usually expressed, the density of gases is small. Some of these differences are not as fundamental as they might at first sight appear, since a gas can be compressed to a liquid, and a liquid converted into a solid. And, similarly, a solid can be liquefied, and a liquid converted into a gas. Indeed, most of the forms of matter with which we are acquainted are known in all three states of aggregation.

Of the three states of aggregation, the gaseous is the simplest, since it represents matter in the most tenuous condition, and will, therefore, be studied first.

Law of Boyle. — The fact that a gas always fills the entire space placed at its disposal makes it easy to change the volume of a gas at will. This can be also accomplished by simply changing the pressure to which the gas is subjected. With increase in pressure the volume of a gas becomes smaller, and with ~~increase~~ in pressure the density of a gas becomes greater. There is a very simple relation connecting these quantities. The pressure of a gas is proportional to its density, and both are inversely proportional to the volume. If we represent the pressure by p, and the density by d,

$$p = cd.$$

If v is the volume and m the mass of the gas, Boyle's law may be expressed thus: —

$$pv = cm.$$

c is a constant for a gas at a given temperature. If p is the pressure and v the volume of a given mass of gas, and p_1 and v_1 the pressure and volume of the same mass of gas under other conditions, Boyle's law may be expressed thus: —

$$pv = p_1v_1.$$

The product of the pressure and volume of a given mass of gas at constant temperature is a constant.

Boyle's law may be expressed in still another way. Since the pressure and density of a gas are proportional, the pressure exerted by a gas varies directly as its concentration, or directly as the number of parts contained in unit volume.

Exceptions to the Law of Boyle. — It was early shown that the law of Boyle does not hold under all conditions. Deviations were observed especially when the gas was subjected to high pressures; the change in volume being less at these pressures than would be supposed from the law of Boyle, as Natterer[1] and others have shown.

The investigation of Amagat[2] on this problem is probably the best, and is certainly the most fundamental which has ever been carried out. He arrived at the same conclusion as that reached by

[1] *Journ. prakt. Chem.* **56**, 127 (1852).

[2] *Ann. Chim. Phys.* [5], **19**, 345 (1880).

Natterer, that the product of pressure and volume, pv, increases with increase in pressure for very high pressures. Amagat plotted the results obtained for hydrogen, nitrogen, carbon dioxide, oxygen, ethylene, etc., in curves.[1] For the smaller pressures the gases were more strongly compressed than would be expected from Boyle's law, —pv decreasing with increase in pressure. The value of pv, with increasing pressure, reached a minimum, conformed closely to Boyle's law for a short range of pressure, and then began to increase as the pressure increased. This will be seen at once from the curves in Fig. 3. Hydrogen, however, is a marked exception. The value of pv increases regularly with increase in pressure from comparatively

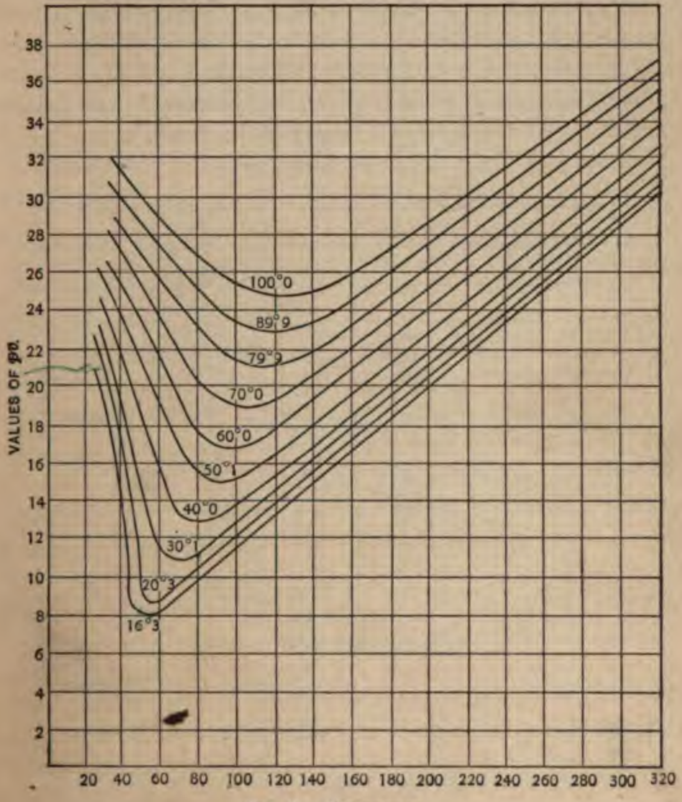

FIG. 3. ETHYLENE.
Pressures in metres of mercury.

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[1] *Ann. Chim. Phys.* **19**, p. 379 (1880).

small pressures, so that the curve for hydrogen does not show any minimum, but is very nearly a straight line. This will be seen from Fig. 4.

Amagat studied also the effect of temperature on the deviations from the law of Boyle. Some of his earlier work[1] indicated that the values of *pv*, with increase in pressure, remained more nearly constant at higher temperatures. This led him to carry out an elaborate investigation, which was published in 1880,[2] and which is probably the most important paper bearing upon the exceptions to Boyle's law. He took a gas, say ethylene, and worked out the values of *pv* with change in pressure at a given temperature. He then found the values of *pv* for the same range in pressure, using a different temperature. In the case of ethylene, the temperatures ranged from 16°.3 to 100°. Amagat used a number of gases, — nitrogen, carbon dioxide, ethylene, marsh gas, and hydrogen, — and plotted the results obtained for each gas at the different temperatures in a curve. The curves for two gases, ethylene and hydrogen, are given in Figs. 3 and 4. The abscissas are the pressures expressed in metres of mercury. The ordinates are the values of *pv*.

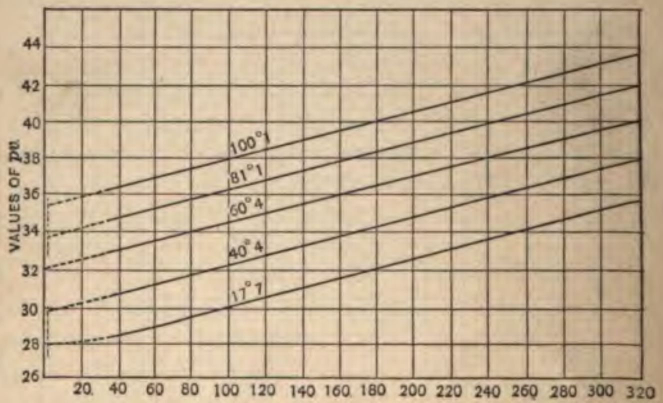

FIG. 4. HYDROGEN.
Pressures in metres of mercury.

The values of *pv* for ethylene and all the other gases studied, with the exception of hydrogen, at first decreased, then reached a minimum, and finally increased as the pressure increased. It will, however, be seen from Fig. 3 that the deviation from the law of Boyle ecomes less and less as the temperature increases. If the law of Boyle applied, the curve would be a straight line parallel to the abscissa. This condition is more and more nearly realized as the temperature rises; and for ethylene at 100° the minimum is far less sharp or pronounced than at 16°.3. The deviation from Boyle's law becomes less and less with rise in temperature also in the case of carbon dioxide and methane, as will be seen by consulting the curves for these gases as worked out by Amagat.[1]

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[1] *Ann. Chim. Phys.* [4], **29**, 246 (1873).

[2] *Ibid.* [5], **22**, 353 (1881), Scientific Memoir Series, V, p. 13.

Hydrogen, as has already been mentioned, is a marked exception. The value of pv increases regularly from the smallest pressure used up to the largest; and further, the curves for different temperatures are very nearly parallel, showing that the deviation from Boyle's law in this case is as great at the higher as at the lower temperature. The question as to the applicability of Boyle's law to gases under very small pressure has also been studied experimentally. The results obtained are so conflicting that it is impossible to decide between them. It, however, seems quite probable that there is no large deviation from Boyle's law shown by very dilute gases; *i.e.* where the pressure is small and there are relatively few gas particles in a given space.

The Law of Gay-Lussac. — If a gas is kept under constant pressure and its temperature raised, the volume will increase. If the volume is kept constant as the temperature rises, the pressure will increase. The remarkable fact has been discovered that the increase in the volume of a gas for a given rise in temperature is a constant, independent of the nature of the gas. All gases increase about $\frac{1}{273}$ ($=0.00367$) of their volume at 0° C. for every rise of one degree in temperature. Gay-Lussac's law states that this temperature coefficient, which we will call B, is constant for all gases. Its exact value is 0.003665.

If we keep the volume constant and warm the gas to $t°$, the pressure P, at this temperature, is calculated from the pressure p_0 at 0°, as follows: —

$$P = p_0\,(1 + 0.003665\,t).$$

If, on the other hand, the pressure is kept constant and the volume allowed to increase with rise in temperature, the volume at $t°$, V, is calculated from the volume at 0°, v_0, thus: —

$$V = v_0\,(1 + 0.003665\,t).$$

If both pressure and volume are allowed to change when the gas is heated, the pressure and volume at $t°$, p and v, are calculated from the pressure and volume at 0° in this manner: —

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[1] *Loc. cit.*

$$pv = p_0v_0\,(1+0.003665\,t)$$

from which, $$v_0 = \frac{pv}{p_0\,(1+0.003665\,t)}.$$

This is the expression generally employed for reducing a gas to what are termed normal conditions. If the volume v of the gas is read at a given pressure, p, and temperature, t, we can calculate at once the volume v_0 at 0° C. and normal pressure p_0 which is taken as 760 mm. of mercury.

The value of the constant 0.003665 is determined either by keeping the pressure constant and measuring the increase in volume with rise in temperature, or by keeping the volume constant and measuring the increase in pressure as the temperature rises. The values found by the two methods differ only slightly, and we take 0.003665 t as very nearly the true value of the temperature coefficient of a gas.

This is very nearly $\frac{1}{273}$, which means that if a gas is cooled down to $-273°$ C. its volume would become zero if the law of Gay-Lussac held down to the limit. This temperature, termed the absolute zero, has now been nearly realized experimentally. It is quite certain that temperatures have been produced which are within twenty degrees of this point. It is, however, very probable that the laws of gas-pressure would not hold at these extreme limits.

If we represent temperature as measured from the absolute zero by T, the combined expression of the laws of Boyle and Gay-Lussac is: —

$$pv = \frac{p_0v_0}{273}\,T.$$

We usually represent $\frac{p_0v_0}{273}$ by R, when the above becomes,

$$pv = RT.$$

Deviations from the Law of Gay-Lussac. — There are many exceptions to the law of Gay-Lussac as well as to the law of Boyle. The coefficient of expansion varies considerably from one gas to another, and varies considerably for the same gas under different temperatures and pressures. This was shown very clearly by the same work of Amagat,[1] in which the exceptions to the law of Boyle were studied. The effect of both temperature and pressure on the coefficient of expansion of ethylene is seen in the following table of results taken from the work of Amagat.[2]

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[1] *Ann. Chim. Phys.* [5], **22**, 353 (1881).

[2] *Ibid.*, p. 383.

Ethylene

PRESSURE IN METRES	20°–40°	40°–60°	60°–80°	80°–100°
30	0.0084	0.0064	0.0046	0.0040
60	0.0366	0.0178	0.0097	0.0067
80	0.0121	0.0195	0.0132	0.0088
100	0.0079	0.0108	0.0121	0.0100
120	0.0062	0.0075	0.0095	0.0082
140	0.0048	0.0062	0.0076	0.0068
160	0.0041	0.0057	0.0061	0.0058
200	0.0034	0.0043	0.0044	0.0044
240	0.0030	0.0035	0.0036	0.0034
280	0.0027	0.0031	0.0030	0.0029
320	0.0025	0.0027	0.0024	0.0024

The horizontal lines show the variation in the coefficient of expansion with change in temperature, the pressure remaining constant. While there is no sharply defined law in this connection, it will be seen from the results that the coefficient increases with the temperature up to a certain point, and then begins to diminish. At higher temperatures the coefficient becomes still less.

The vertical columns, however, bring out a well-defined relation between the coefficient of expansion at a definite temperature and the pressure. The coefficient increases with the pressure to a maximum and then decreases regularly. If we examine the curves for ethylene (Fig. 3), we will see that the maximum value of the coefficient of expansion corresponds closely to the pressure at which the value of pv is a minimum. As the temperature rises this maximum becomes less and less sharply defined, just as the minimum for pv becomes less sharply defined.

The decrease in the coefficient of expansion with rise in temperature beyond a certain point is also shown by the curves in Fig. 3. The distance between the curves for any given pressure becomes less and less as the temperature rises.

The applicability of the law of Gay-Lussac to gases under very small pressure has been studied by a number of experimenters. The work of Baly and Ramsay[1] should, however, receive special notice. They worked with a number of gases, from a few millimetre's pressure down to a very small fraction of a millimetre. The pressure used with hydrogen varied from 4.7 mm. to 0.077 mm. The coefficient of expansion at the higher pressure was $\frac{1}{273.5}$. This remained practically constant until the pressure was diminished to 0.4 mm. When still further diminished the coefficient of expansion decreased and was only $\frac{1}{300.5}$ at a pressure of 0.077 mm. Oxygen behaves very differently from hydrogen. Its coefficient of expansion at 5.1 mm. is $\frac{1}{261}$, which is larger than would correspond to the law of Gay-Lussac. It increases with decrease in pressure, being $\frac{1}{251}$ at 2.5 mm., and at 0.07 mm. it is about $\frac{1}{240.3}$. With nitrogen we find at 5.3 mm. that the coefficient of expansion is $\frac{1}{304}$, being much less than would be expected from the law of Gay-Lussac. This value becomes still less as the pressure decreases, being only $\frac{1}{331}$ at a pressure of 0.8 mm.

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[1] *Phil. Mag.* **38**, 301 (1894).

The law of Gay-Lussac, like the law of Boyle, must be regarded as an approximation, which holds rigidly only under special conditions. There are many exceptions known to both laws, but those already considered suffice to show the general character of the exceptions most frequently met with.

The Law of Avogadro. — The law of Avogadro has been already referred to in connection with the determination of the molecular weights of vapors. It will be recalled that the law was proposed to account especially for the simple volume ratios in which gases combine, and the simple ratios between the volumes of the constituents and those of the products formed. The law is usually stated thus: equal volumes of all gases at the same temperature and pressure contain the same number of ultimate parts. This law cannot be proved directly by experiment, but is in accord with so many facts that it is very probably true. Indeed, it has been tested, indirectly, in so many directions that it is now given a place among the laws of nature. It is true, however, that it does not seem to hold absolutely in some cases. Thus, two volumes of hydrogen do not combine with exactly one volume of oxygen to form water. We must, therefore, assume either that water is not H_2O, or that the law of Avogadro does not hold rigidly in this case. The latter assumption is, of course, by far the most probable, and is therefore the one accepted.

We can combine the three laws of gas-pressure in one expression,[1] just as we combined the two laws, those of Boyle and Gay-Lussac, in the equation $PV = RT$.

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[1] Horstmann: *Ber. d. chem. Gesell.* **14**, 1242 (1881). Van't Hoff: *Ztschr. phys. Chem.* **1**, 491 (1887), Scientific Memoir Series, IV. p. 24.

Let us deal with gram-molecular weights[1] of gases. The pressure exerted by a gram-molecular weight of a gas at 0° C., in the space of a litre, is about 22.4 atmospheres. If we use the equation —

$$pv = \frac{p_0 v_0}{273} T,$$

and substitute for p_0 the above pressure, and for v_0 the value 1, we have —

$$\begin{aligned} pv &= \frac{22.4}{273} T \\ &= 0.082\ T. \end{aligned}$$

This is the combined expression of the laws of Boyle, Gay-Lussac, and Avogadro.

Apparent Exceptions to the Law of Avogadro. — There are a number of substances known which, for a time, were regarded as exceptions to the law of Avogadro. The densities of their vapors were smaller than would be expected from the law of Avogadro. Among these substances are ammonium chloride, ammonium cyanide, ammonium sulphide, ammonium hydrosulphide, phosphorus pentachloride, and chloral hydrate. It has, however, been shown that these compounds are not exceptions to the law of Avogadro, but agree very well with it. The very small vapor-densities are satisfactorily explained, as will be seen when we come to deal with this phase of our subject.

THE KINETIC THEORY OF GASES

The Kinetic Theory. — We have considered thus far the laws to which the pressure of gases conforms, and have found that gases in general obey approximately the laws of Boyle, Gay-Lussac, and Avogadro. The question has thus far not been raised, why a gas exerts any pressure at all. It is more than probable that the pressure exerted by all gases is due to the same cause, since different gases obey so nearly the same laws of pressure. Further, the nature of these laws makes it highly probable that the structure of gases is comparatively simple, and the nature of gas-pressure, mechanically considered, not very complex.

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[1] A gram-molecular weight is the molecular weight of the gas in grams.

The theory which has been proposed to account for gas-pressure is known as the kinetic theory. According to this theory, the particles or molecules of a gas are continually moving in all directions in straight lines; the velocity being very great, and each particle moving independently of all others. These particles would frequently strike one another and also the walls of the containing vessel, and thus the pressure of gases would be produced. The pressure of the gas on the walls of the confining vessel is then due to the blows or impacts of the gas particles against these walls.

Deviations from the Gas Laws explained by the Kinetic Theory. Van der Waals' Equation. — We have seen that the laws of gas-pressure are only approximations and hold only under very special conditions. We will now examine gases in the light of the kinetic theory and see whether any explanation of the exceptions to the gas laws can be found. If gas-pressure is due to the impacts of the gas particles against the walls of the vessel, the space in which these particles move is evidently not the whole volume of the gas, as we have thus far assumed, but is not greater than the volume of the gas minus the space occupied by the particles themselves. If the pressure is small, or what amounts to the same thing, the volume large, there are relatively few particles in a large space, and the space occupied by the particles themselves is so small compared with the spaces between the particles that it is negligible. If the gas is under high pressure there are many more particles in a given volume, and the space occupied by the gas molecules themselves becomes quite considerable. We have seen that the gas laws hold much more closely when the gas is dilute or under small pressure, than when the pressure is great. It is, therefore, evident that we must take into account the space occupied by the gas molecules themselves. We must introduce into the equation which expresses both the laws of Boyle and Gay-Lussac ($pv = RT$) a factor for the volume of the gas molecules. If we call this factor, which is a constant for every gas, b, the above equation becomes —

$$p(v-b) = RT.$$

There is one factor, however, which is still not taken into account. The assumption is made that the particles of gas do not exert any attraction upon one another, and it is quite certain that such an attraction exists. Van der Waals[1] has taken this into account, and has modified the gas equation accordingly. The attraction exerted by the gas particles is proportional to the specific attraction a, and inversely proportional to the square of the volume v. This term $\frac{a}{v^2}$ must be added to the pressure p, since the attraction of particles for each other has the same effect as subjecting the gas to an increase in pressure. Van der Waals' equation is then —

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[1] *Die Kontinuität des gasförmigen und flussigen Zustandes*, Leipzig, 1881.

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT.$$

This equation explains many of the exceptions shown by gases to the simpler laws of Boyle and Gay-Lussac. If the pressure is small, $\frac{a}{v^2}$ becomes negligible because of the large value of v, and b the space occupied by the molecules is also small. The gas under these conditions would be more likely to accord with the simpler expressions, and such is in general the fact, with perhaps a few exceptions at very small pressures, and here experimental errors are large. As the pressure increases the two correction terms acquire finite values, but act in opposite senses. If a has a large value, the volume is appreciably diminished, and pv decreases, as is shown in the curves for ethylene (Fig. 3). As the pressure still further increases, a becomes relatively smaller with respect to p, and the influence of b begins to manifest itself. The gas becomes relatively less compressible, or pv increases with the pressure. This is also seen in the curves for ethylene. The two correction terms have the same value at a pressure of from 40 to 100 m. of mercury depending upon the temperature, and at this pressure the gas obeys the simpler expression of Boyle's law.

In the case of hydrogen (Fig. 4), the value of pv continually increases with the pressure. This means that the value of the constant a is so small that it is more than counterbalanced by b at all pressures. The determination of the values of the constants a and b for any gas is comparatively simple. Reference only can be given here to the methods[1] which are used. The exceptions to the laws of Boyle and Gay-Lussac, which were pointed out when these laws were considered, are, then, fully explained by means of the kinetic theory of gases.

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[1] Ostwald: *Lehrb. d. Allg. Chem.* I, p. 226.

DENSITIES AND MOLECULAR WEIGHTS OF GASES

Densities and Molecular Weights. — The determination of the relative densities of gases consists in determining the relative weights of equal volumes of gases at the same temperature and pressure. Since equal volumes of gases under the same conditions contain an equal number of molecules, the densities stand in the same relation as the molecular weights. Thus, by means of Avogadro's law we can determine the molecular weights of substances in the gaseous state.

Some substance must be taken as the unit in determining the densities in gases. Air has generally been selected as the unit, and the weights of equal volumes of other gases, at the same temperature and pressure, compared with that of air. Hydrogen has also been used as the unit, and is to be preferred to air, since the composition of the latter varies slightly from time to time and from place to place. The density of air is 14.37 times the density of hydrogen, and since the molecular weight of hydrogen is 2, we must multiply the density referred to air as the unit by 28.74, to obtain the molecular weight of the gas. If we represent the molecular weight of the gas by m, and the density referred to air as the unit by d,

$$m = d \times 28.74.$$

In this way the molecular weights of gases can be calculated from their densities.

A number of methods and a large number of modifications of methods have been proposed for determining the densities of gases. The more important will be briefly considered.

Method of Dumas. — The method of Dumas[1] consists in determining the amount of substance which in the form of vapor, at a given temperature, just fills a flask whose volume is afterwards determined. The flask is weighed full of air. Knowing the volume of the flask, we know the weight of air contained in it; therefore we know the weight of the empty flask. The weight of the flask being known, and the weight of the flask plus the substance which just filled it with vapor, we know the weight of the substance. By determining the weights of the vapors of different substances which fill a flask of given volume, we have the relative densities of the vapors.

The apparatus used is a balloon flask (Fig. 5) holding from 100 to 250 cc.

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[1] *Ann. Chim. Phys.* [2], **33**, 337 (1826).

The flask is carefully dried and weighed, using as a tare another flask of very nearly the same size. We are in this way made independent of the conditions of temperature, moisture, etc., under which the weighing is made.

A few grams of the substance whose vapor-density is to be determined are introduced into the flask, the neck drawn out to a capillary, and the flask placed in a bath which is at least ten or fifteen degrees above the boiling-point of the substance. The substance vaporizes, drives out the air, and when the vapor of the substance ceases to escape, the capillary is fused shut. The flask after cooling is weighed. The fine point is then cut off under mercury and the flask filled with mercury. The flask may then be weighed again, or the mercury poured out and measured, giving the volume of the flask.[1]

The method of Dumas is not as well adapted to higher temperatures as other methods to be considered later. In the first place, it is difficult to measure high temperatures accurately; and, further, the amount of substance contained in the bulb at high temperatures is so small that relatively large errors result from this source. Deville and Troost[2] have used this method at fairly high temperatures, employing porcelain balloons, but their results are not very accurate. The method of Dumas cannot be used with even a fair degree of accuracy above 600° to 700° C.

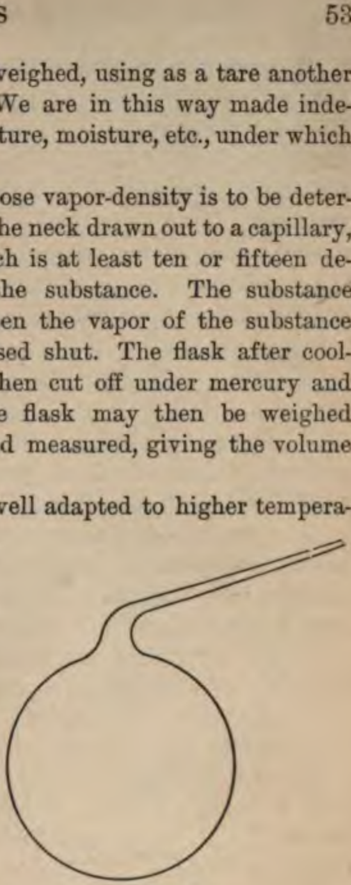

FIG. 5.

An attempt has been made to use the Dumas method under diminished pressure. Habermann[3] has so arranged the bulb that a low pressure can be maintained constant, and the pressure read on a manometer. Larger bulbs are required for work under diminished pressure, and even then the quantity of substance is so small that considerable errors are introduced.

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[1] For details in carrying out the method and calculating the results, see Kohlrausch: *Leitfaden der Praktischen Physik*, p. 69. Biltz: *Practical Methods for Determining Molecular Weights;* translated by Jones and King, p. 40. Also, Traube: *Physikalisch-chemische Methoden*, pp. 25–27.

[2] *Ann. Chim. Phys.* [3], **58**, 257 (1860).

[3] *Lieb. Ann.* **187**, 341 (1877).

A large number of modifications of the method of Dumas have been proposed,[1] but that of Bunsen[2] should be especially mentioned. He used three vessels of the same volume and weight. One was empty, one was filled with air at a given temperature and pressure, and the third was filled with the vapor at the same temperature and pressure. If we represent by W_1 the weight of the vessel filled with the vapor, by W_2 the weight of the vessel filled with air, and by W_3 the weight of the vessel in which there is a vacuum, the relative density of the vapor and air is expressed thus: —

$$\frac{W_1 - W_3}{W_2 - W_3}.$$

After vessels of the same volume and weight have once been prepared, this method of procedure is more convenient and far more rapid than that originally described by Dumas.

The method of Dumas is used less to-day than it was formerly, having been largely supplanted by better methods, especially at elevated temperatures. The apparatus used in this method is, however, exceedingly simple, and even at present the Dumas method is employed in certain cases where the presence of a foreign gas in the vapor must be avoided.

The Method of Gay-Lussac. — The method devised by Gay-Lussac[3] for determining the densities of vapors is based upon a principle which is quite different from that which we have just considered. In the method of Dumas the vapor required to fill a given volume was weighed. In the method of Gay-Lussac a weighed amount of substance is converted into vapor, and the volume of the vapor measured. The method as originally proposed by Gay-Lussac consists in placing a known weight of liquid in a calibrated vessel over mercury. The whole is then warmed until the liquid is converted into vapor. The temperature is noted, also the volume of the vapor. The latter is reduced to standard conditions, a correction being introduced for the tension of the mercury vapor. This method has been so greatly improved that the original is no longer used.

Hofmann's Modification of the Gay-Lussac Method. — The modification of the Gay-Lussac apparatus proposed by Hofmann[4] consists in elongating the inner tube beyond the barometric height so that a vacuum will exist in the top of the tube. The substance is introduced into the tube over the mercury and volatilized under diminished pressure. The apparatus is shown in the following figure.

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[1] Buff: *Pogg. Ann.* **22**, 242 (1831). Marchand: *Journ. prakt. Chem.* **44**, 38 (1848). Victor Meyer: *Ber. d. chem. Gesell.* **13**, 399, 2019 (1880).

[2] *Gasomet. Methoden*, second edition, p. 154.

[3] Biot: *Traité*, I, p. 291.

[4] *Ber. d. chem. Gesell.* **1**, 198 (1868); **9**, 1304 (1876).

The calibrated tube *A* rests in a mercury reservoir *R*, and is more than 76 cm. long. It is fastened into a vapor-jacket *J* into which vapor enters at *a*, and leaves at *b*. *m* is a bar of metal terminating in an adjustable point, which is brought down to the surface of the mercury; the cross-hairs attached to the bar at *h* serving to read more accurately the height of the mercury in the tube *A*.

After the substance is converted into vapor the volume of the vapor is read and reduced to standard conditions. Knowing the weight of the substance and the volume of vapor, the density of the vapor is calculated at once. The advantage of the modification proposed by Hofmann is that the substance is converted into vapor at a temperature below its boiling-point under atmospheric pressure. Thus, the vapor-density of many substances which would decompose if boiled under atmospheric pressure can be determined. Indeed, Hofmann devised this method especially for use with organic substances which would easily decompose.

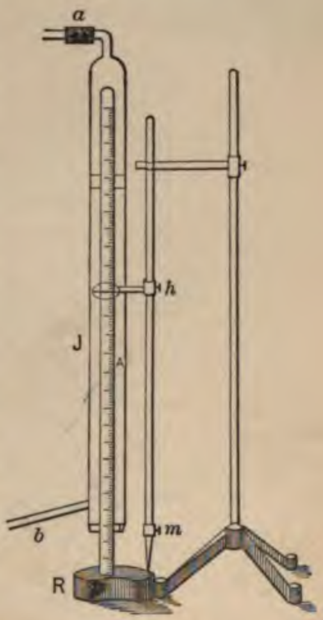

Fig. 6.

The Gas-displacement Method of Victor Meyer. — A method of determining vapor-densities was devised by Victor Meyer[1] in 1878, which has practically supplanted all other methods, except in very special cases. The method consists in volatilizing a small weighed portion of substance in a tube filled with air, and collecting and measuring the volume of air which is displaced.

The apparatus used is seen in Fig. 7. The inner vessel *A* is surrounded by a glass jacket *J*, in which is boiled some substance which will heat *A* to a constant temperature, and at the same time to the temperature desired. The tube *A* is closed above with a

[1] *Ber. d. chem. Gesell.* **11**, 1867, 2253 (1878).

stopper, and from the central tube a side tube runs over to, and under, a calibrated tube filled with water and dipping into a water reservoir. The substance to be used is weighed in a weighing tube which is closed loosely at the top, and introduced, when desired, into the top of *A*. In carrying out a determination, a liquid which has a higher boiling-point than the substance whose vapor-density is to be determined is placed in the outer jacket. This liquid is boiled, and a part of the air in the inner vessel is driven out. When no more air escapes from the side-tube, the tube containing a weighed amount of substance is introduced into the top of *A*, and rests on the rod *r*. When temperature equilibrium has been perfectly established, the mouth of the side-tube is placed under the measuring tube in the water tank, the rod *r* drawn back, and the small vessel containing a weighed amount of the substance allowed to drop to the bottom of *A*. The substance volatilizes, drives out the loosely fitting cork from the weighing tube, and then displaces air from the tube *A*. The displaced air is received in the measuring tube *t*, and its volume is equal to the volume of vapor formed in the tube *A* by the known weight of the substance introduced. We know the amount of substance used, also the volume of the air displaced, which is equal to the volume of vapor formed; consequently the density of the vapor of the substance.

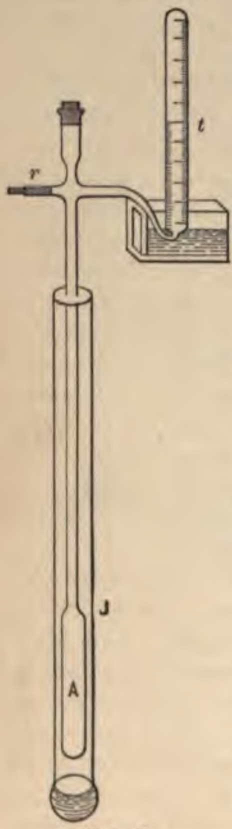

Fig. 7.

A very small amount of substance suffices for determining vapor-density by this method, and the method can be used at very high temperatures. At higher temperatures vessels of glass cannot of course be employed, but porcelain can be used. Berlin porcelain can be employed up to 1600°, and other more resistant forms of porcelain[1] can be used up to 1700°, or perhaps a little higher. Platinum vessels can be used up to 1700°. There is no material known which can be used above 1800°.

The great advantage of this method, in addition to the small amount of substance required, is that the temperature of the experiment does not need to be known. It is only necessary to keep the temperature constant before and after the introduction of the substance. The gas-displacement method is so far superior to all others at high temperatures that it has practically supplanted them all.

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[1] Biltz: *Ztschr. phys. Chem.* **19**, 406 (1887).

It is not necessary to fill the vessel *A* with air. This may be replaced by an indifferent gas, in case the oxygen of the air would act chemically upon the substance to be vaporized. Thus, if we were determining the vapor-density of arsenic or sulphur, oxygen must be excluded, and the vaporizing vessel could be filled with nitrogen or hydrogen. If the vapor of magnesium was being studied, nitrogen could not be used, since it would act chemically upon the magnesium.

The gas-displacement method of Victor Meyer has also been used under diminished pressure,[1] and the vapor-densities of substances determined considerably below their boiling-points. The advantage of increased stability of the substance at the lower temperature has already been mentioned. A number of modifications of Meyer's method have been devised for working at diminished pressures. La Coste[2] places the whole apparatus under diminished pressure. Lunge and Neuberg[3] also work at known pressure, while Traube[4] reads the volume of displaced air at the diminished pressure of the experiment. Bleier[5] devised an ingenious manometer for measuring accurately very small pressures, and together with Kohn determined the vapor-density of sulphur at very small pressures.

Method of Bunsen. — Bunsen[6] has devised a rough method of determining the relative densities of gases. Gases under the same pressure pass through a small opening with velocities which are inversely as the square roots of their densities. The method consists in allowing equal volumes of different gases to pass through a very fine hole in a platinum plate, which covers the top of the cylinder containing the gas, and noting the time required. The cylinder is immersed in mercury, which enters from below as the gas escapes at the top. The method is not capable of any very great refinement, and the results obtained by means of it are only close approximations.

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[1] *Ber. d. chem. Gesell.* **23**, 311 (1890). Bleier: *Monatsh.* **20**, 505, 909 (1899); **21**, 575 (1900).

[2] *Ber. d. chem. Gesell.* **18**, 2122 (1885).

[3] *Ibid.* **24**, 729 (1891). See Traube: *Physikalisch-chemische Methoden*, p. 34.

[4] *Physikalisch-chemische Methoden*, p. 34.

[5] *Monatsh.* **20**, 909 (1900).

[6] *Gasomet. Method.*, p. 160.

Of the methods considered for determining the densities of vapors, that of Meyer is by far the most generally applicable. The method of Gay-Lussac and the modification proposed by Hofmann are seldom used. The method of Dumas is used at present only in special cases, to which reference will be made in detail a little later.

Results of Vapor-density Measurements. — The vapor-densities of elementary gases have shown many interesting and surprising relations between the number of atoms contained in the molecules of these substances. The molecular weights of a number of elementary gases, calculated from their densities, show that the molecule is made up of two atoms. This applies to hydrogen, oxygen, nitrogen, chlorine, bromine, and a number of others. The vapor-densities of mercury, cadmium, and glucinum show that the molecule is monatomic, or that the molecule and atom are identical. On the other hand, the molecules of phosphorus, sulphur, etc., contain more than two atoms, if the temperature to which they are heated is not too high.

The vapor-density, and, therefore, the number of atoms contained in the molecule, varies in some cases with the temperature. Take the case of sulphur. The vapor-density at about 500° C. gives a molecular weight which is about six times the atomic weight of sulphur; or, in a word, at this temperature the molecule of sulphur consists of six atoms. The vapor-density of sulphur at about 800° shows a molecular weight of 70, and at about 1100° of approximately 64. The molecule of sulphur, which contains six atoms at the lower temperature, has therefore broken down at the higher temperature into three molecules, containing two atoms each.

Similar results were obtained with phosphorus. At 500° C. there are four atoms in the molecule. The vapor-density becomes continually less with rise in temperature, until at about 1700° C. the molecule of phosphorus contains only three atoms.

The case of iodine is especially interesting. At temperatures from 200° to 600° the molecule of iodine consists of two atoms. As the temperature rises, V. Meyer[1] on the one hand, and Crafts and F. Meier[2] on the other, found that the vapor-density decreases, and that above 1400° the density is only about one-half the value at the lower temperature. Above 1600° it is quite certain that the vapor-density of iodine would remain constant, since at this temperature the atom and molecule would be identical, and no further dissociation of the molecules could take place.

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[1] *Ber. d. chem. Gesell.* **13**, 394, 1010 (1880).

[2] *Ibid.* **13**, 851 (1880). *Compt. rend.* **92**, 39 (1881).

This dissociation of more complex into simpler molecules is not limited to elementary gases. The molecule of arsenious oxide from 500°–700° is shown by its vapor-density to have the composition As_4O_6. As the temperature rises, the vapor-density becomes less and less, and at 1800° it corresponds to the simpler formula As_2O_3. Similarly, vapor-density methods make it very probable that the molecules of ferric chloride and aluminium chloride correspond to the double formulas at lower temperatures; and that these more complex molecules break down into the simplest molecules, $FeCl_3$ and $AlCl_3$, as the temperature rises.

In working either with elementary gases or with the vapors of compounds which undergo dissociation, the method of Dumas is greatly to be preferred to that of Meyer, since in the latter there is always present a considerable quantity of some foreign gas, which affects the amount of dissociation. This foreign gas dilutes the vapor whose density is being determined, and it is well known that this will change the amount by which the vapor will be dissociated. This accounts for the difference between the results obtained in such cases by the gas-displacement method and the method of Dumas.

Abnormal Vapor-densities. Apparent Exceptions to the Law of Avogadro. — The vapor-densities of the elementary substances mentioned above showed that the molecules of some vapors contain a number of atoms, the molecules of others two atoms, while in some vapors at low temperatures, and in others at higher temperatures, the molecule contains one atom, or the molecular weight is identical with the atomic weight. In the case of no elementary substance, however, was the molecular weight found from vapor-density less than the atomic weight of the element, and in none of the compounds thus far mentioned was the molecular weight less than the sum of the atomic weights of the elements entering into the compound. In a number of cases the molecular weight showed that the molecule of the compound was the simplest possible, but there was nothing to indicate that the simplest molecule had in any case broken down into its constituents. We must now turn to another class of phenomena. The molecular weights of substances like ammonium chloride, phosphorus pentachloride, choral hydrate, etc., calculated from their vapor-densities, were less than the sum of the atomic weights of their constituent elements. Thus, the vapor-density of ammonium chloride, corresponding to the formula NH_4Cl must be 1.89, while Bineau[1] found the value 0.89. The vapor-density of phosphorus pentachloride of the formula PCl_5 must be 7.20. Neumann[1] found by the method of Dumas at 182° the value 5.08. This decreased with rise in temperature up to 290°, where it became constant at 3.7. Similar results were found by Cahours.[2] A number of other examples similar to the above were known, but these suffice to illustrate the point. The explanation of these abnormal results was not furnished at once, and for a time the hypothesis of Avogadro was rather at a discount because of their existence. The explanation, however, has been furnished, as we shall now see, and the law of Avogadro thoroughly substantiated.

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[1] *Ann. Chim. Phys.* [2], **68**, 440 (1838).

Explanation of the Abnormal Vapor-densities. — After Deville[3] had shown in 1857 that many chemical compounds are broken down or dissociated by heat, it occurred to Cannizzaro,[4] Kopp,[5] and others, that the abnormal vapor-densities of substances like ammonium chloride, phosphorus pentachloride, etc., might be due to the dissociation of these substances by heat. If a substance like ammonium chloride was dissociated, one molecule would yield one molecule of ammonia and one of hydrochloric acid. One molecule of phosphorus pentachloride would break down into one molecule of phosphorus trichloride and one molecule of chlorine. If such a dissociation did take place, it would account for the abnormally small vapor-densities found, since the substances in the form of vapor would occupy a greater space than if there was no dissociation. But this did not prove that such a dissociation actually took place. How could this point be tested?

Take the case of ammonium chloride; if it is dissociated by heat, it would yield ammonia and hydrochloric acid in equivalent quantities. It would, however, be exceedingly difficult, if not impossible, to detect either ammonia or hydrochloric acid when the two gases were mixed in equivalent quantities. This problem was solved by Pebal.[6] He made use of the different rates at which these two gases diffuse to separate them, in part, in case they were present in the vapor of ammonium chloride. The apparatus which he used is seen in Fig. 8. The ammonium chloride *d*, rests on a plug of asbestos *c*, near the top of the inner tube, which is open above. A stream of hydrogen is passed through *a* into the outer part of the apparatus, and another stream through *b* into the inner part of the apparatus. The whole is heated above the boiling-point of ammonium chloride. If the salt is decomposed when it volatilizes, the ammonia being lighter than the hydrochloric acid would diffuse more rapidly through the plug of asbestos. The vapor in the inner tube below the plug would therefore contain an excess of ammonia. This vapor is swept out by means of the stream of hydrogen gas, and made to pass over a piece of moist red litmus paper in the vessel *B*. It was found that this was colored blue, proving the presence of an excess of ammonia.

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[1] *Lieb. Ann. Suppl.* **5**, 341 (1867).
[2] *Ann. Chim. Phys.* [3], **20**, 373 (1847).
[3] *Compt. rend.* **45**, 857.
[4] *Nuovo Cimento*, **6**, 428.
[5] *Lieb. Ann.* **105**, 390 (1858).
[6] *Ibid.* **123**, 199 (1862).

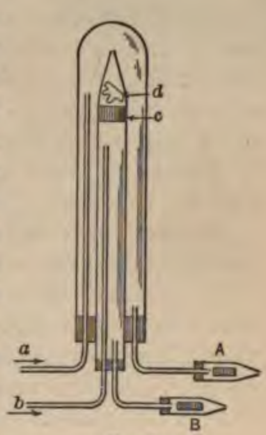

FIG. 8.

The vapor remaining in the inner tube above the wad of asbestos must contain an excess of hydrochloric acid, since more ammonia has passed through the asbestos than hydrochloric acid. This is swept out by means of the stream of hydrogen in the outer vessel, and passed over a piece of blue litmus in the vessel *A*. This turned red at once, showing the presence of free hydrochloric acid in this gas. It would seem, then, that Pebal had demonstrated beyond doubt that the vapor of ammonium chloride contains both free ammonia and free hydrochloric acid, and, therefore, that this substance is dissociated by heat.

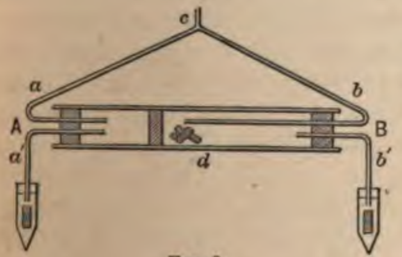

FIG. 9.

The objection was, however, raised to the experiment of Pebal, that a foreign substance, asbestos, had been used in contact with the vapor of ammonium chloride, and that this might have caused the vapor to dissociate, or at least might have facilitated the breaking down of the salt by heat. This objection, while apparently having but little foundation, could not be ignored. To test this point Than[1] devised the following apparatus (Fig. 9): The tube *AB*, in which the ammonium chloride is contained, is placed horizontally, and the septum is made out of ammonium chloride. Nitrogen is passed through the tube, the ammonium chloride *d* heated with a lamp, and the vapors in the two sides passed over colored litmus, as in the experiment of Pebal. The vapor in the side next to the ammonium chloride was found to contain free hydrochloric acid, and free ammonia was shown to be present in the vapor which had diffused through the plug of ammonium chloride.

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[1] *Lieb. Ann.* **131**, 129 (1864).

It is thus shown beyond question that the vapor of ammonium chloride is broken down, in part, into ammonia and hydrochloric acid, by heat alone.

The work of Wanklyn and Robinson[1] has shown that phosphorus pentachloride is dissociated by heat into the trichloride and chlorine. The pentachloride was placed in a short-necked glass flask, in which it was to be converted into vapor. Over the neck of this flask a wider glass tube was placed, so that the two were separated by an air-space. Air was passed in through the upper tube and escaped through the space between the two glass tubes. If the vapor of the pentachloride was dissociated by heat into the trichloride and chlorine, these would diffuse with different velocities into the upper portion of the vessel, since they have different vapor-densities. They would then be swept out by the current of air in different quantities, the chlorine being in excess since it is the lighter, and would, therefore, diffuse more rapidly into the upper portion of the vessel.

Free chlorine was proved to be present in the vapors which escaped, and analysis showed an excess of phosphorus trichloride remaining in the flask. Therefore, the phosphorus pentachloride was broken down, in part at least, by heat into its constituents. This conclusion was confirmed by the observation that as the vapor of phosphorus pentachloride is heated higher and higher it becomes colored more deeply greenish yellow, — the characteristic color of chlorine itself.

The vapor of chloral hydrate — $CCl_3\,COH\,.\,H_2O$ — was shown by Würtz[2] to contain water-vapor. Dehydrated potassium oxalate absorbed water from the vapor of this substance, and thus diminished its vapor-tension very considerably.

It was thus shown that the compounds, ammonium chloride, phosphorus pentachloride, and chloral hydrate, are dissociated by heat. The abnormal vapor-densities are then satisfactorily accounted for, and instead of these substances presenting any real exceptions to the law of Avogadro, they furnish a beautiful confirmation of the law.

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[1] *Compt. rend.* **52**, 549; *Journ. prakt. Chem.* **88**, 490 (1863).

[2] *Compt. rend.* **84**, 977 (1877); **86**, 1170 (1878).

The same explanation undoubtedly applies to other substances whose vapor-densities are abnormally small. They are more or less broken down by heat into their constituents; the amount of the dissociation increasing with the temperature.

Dissociation of Vapors diminished by an Excess of One of the Products of Dissociation. — A discovery was made in connection with the study of dissociating vapors, which has proved to be of the very highest importance. If there is present an excess of either of the products of dissociation, the amount of the substance decomposed is lessened. Thus, ammonium chloride is less dissociated if there is present an excess of either ammonia or hydrochloric acid. Similarly, phosphorus pentachloride is much less decomposed at a given temperature if there is present an excess of either phosphorus trichloride or chlorine, as Würtz[1] has shown. Indeed, the vapor of phosphorus pentachloride is scarcely dissociated at all by heat in the presence of an atmosphere of phosphorus trichloride, or of chlorine. The vapor-density of phosphorus pentachloride in an atmosphere of the trichloride was found to be about 209, while the calculated vapor-density is 208.

This is a perfectly general principle, illustrated by phosphorus pentachloride and ammonium chloride. The dissociation of substances in general by heat is driven back by an excess of any one of the products of dissociation. This is the first example thus far met with of the effect of mass on chemical activity. The importance of the action of mass will be more clearly seen as the subject develops.

SPECIFIC HEAT OF GASES

Specific Heats at Constant Pressure and at Constant Volume. — The amount of heat required to produce a given rise in temperature in equal quantities of different gases, under the same conditions, varies from gas to gas. This is usually expressed by saying that each gas has its own definite capacity for heat. If we represent the amount of heat added by $d\theta$, and the rise in temperature by dt, the heat capacity c is expressed thus: —

$$c = \frac{d\theta}{dt}.$$

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[1] *Compt. rend.* **76**, 601.

The heat capacities of unit quantities of gases are termed their specific heats. If we represent unit mass by m, the specific heat C is expressed thus: —

$$C=\frac{1}{m}\frac{d\theta}{dt}.$$

The specific heat of a gas has been found to vary greatly with the pressure. If the gas is allowed to expand as it is heated, so that the pressure remains constant, it has a definite specific heat, which is termed its specific heat at constant pressure. This is usually represented by C_p. If, on the contrary, the volume of the gas is kept constant as the temperature rises, — the pressure increasing, — the gas has a different specific heat. This is termed its specific heat at constant volume, and is usually written C_v.

These two specific heats for the same gas are very different, as we shall see, and we must always carefully distinguish between them.

Determination of Specific Heats at Constant Pressure and at Constant Volume. — The gas is warmed to a known temperature and then allowed to flow through a tube surrounded by water in a carefully protected calorimeter. The original and final temperatures of the gas and its mass being known, also the mass, specific heat, and rise in the temperature of the water, we have the data necessary for calculating the specific heat of the gas under constant pressure. In connection with the specific heat of gases at constant pressure, we should mention especially the older work of Regnault[1] and the more recent work of E. Wiedemann.[2]

Regnault found that the specific heat of a number of gases, such as oxygen, hydrogen, etc., was a constant, independent of the temperature, while the specific heat of carbon dioxide changed very considerably with the temperature. That the specific heat of gases is somewhat dependent upon the temperature has been shown by the more recent work of Le Chatelier[3] and others. The specific heats of different gases tend more nearly to the same value, the lower the temperature.

A few of the results of Regnault are given below. These are calculated, not for equal amounts of the different gases, but for quantities which bear the same relation to one another as the molecular weights. These are known as "molecular heats."

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[1] Paris, 1862.

[2] *Pogg. Ann.* **157**, 1 (1876). *Wied. Ann.* **2**, 195 (1877).

[3] *Compt. rend.* **93**, 962 (1881). Beibl: *Wied. Ann.* **14**, 364 (1890). ***Ztschr. phys. Chem.*** **1**, 456 (1887).

	Molecular Weight	Molecular Heat at Constant Pressure
Oxygen, O_2	32	6.96
Nitrogen, N_2	28	6.83
Hydrogen, H_2	2	6.82
Chlorine, Cl_2	70.9	8.58
Hydrochloric acid, HCl	36.5	6.68
Carbon dioxide, CO_2	44.0	9.55
Hydrogen sulphide, H_2S	34.0	8.27
Carbon bisulphide, CS_2	76.0	11.93
Benzene, C_6H_6	78.0	29.28
Ether, $C_4H_{10}O$	74.0	35.50
Acetone, C_3H_6O	58.0	23.92
Stannic chloride, $SnCl_4$	259.8	24.39

E. Wiedemann improved the method of Regnault in a number of ways. With less elaborate apparatus he was able to obtain as satisfactory results as Regnault had done. Instead of using such a long tube and large calorimeter through which the gas must pass to restore temperature equilibrium, he filled the tube with silver turnings.[1] This offered a larger surface to the gas, and temperature equilibrium was established in a much shorter tube. The results of Wiedemann's investigations are quite as accurate as Regnault's. He also found that the specific heats of gases are somewhat dependent upon the temperature.

To measure directly the specific heats of gases at constant volume, the gas must be placed in a vessel which will withstand great pressure without change in volume, and the gas and vessel must be heated to the desired temperature. The gas and vessel must then be introduced into the calorimeter. A moment's reflection will show that the heat given out by the vessel will be much greater than that by the gas, and, therefore, all experimental errors will accumulate on the comparatively small quantity of heat given up to the calorimeter by the gas when it cools. For this reason accurate measurements of the specific heats of gases at constant volume are impossible. It, however, has been found that the specific heat at constant volume is always less than at constant pressure.

The specific heats of gases at constant volume have, however, been calculated from the specific heats at constant pressure by the aid of thermodynamics. Instead of using specific heats referred to equal weights of gases, molecular heats have been employed, and an unusually interesting and important relation between the molecular heats at constant pressure and the molecular heats at constant volume has been discovered. We will now follow in some detail the method by which this relation has been pointed out.

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[1] *Wied Ann.*, **157**, 1 (1876).

The Mechanical Theory of Heat and the Mechanical Equivalent of Heat. — Before attempting to deduce any relation between the specific heat at constant pressure and the specific heat at constant volume, we should raise the question as to why there should be any difference between the two; and further, why should the specific heat at constant pressure be greater than at constant volume?

If we inquire into what takes place when a gas is warmed, on the one hand at constant pressure, and on the other at constant volume, we would be impressed at once by this difference. When a gas is heated at constant pressure, it expands, occupying a larger volume. In expanding it must drive back the air, or, as we say, do work. When a gas is heated at constant volume it cannot expand, and, therefore, does not do external work. There is thus a marked difference in the conditions under which the gas is warmed.

If heat were consumed in doing work, then we could understand why the amount of heat required to raise the temperature of a gas a given amount was greater at constant pressure than at constant volume. And since, under the same conditions, a gas always gives out the same amount of heat when cooled over a certain range in temperature, as was required to raise it over this same range of temperature, we could see why the specific heat at constant pressure would be greater than the specific heat at constant volume.

As is well known, this is exactly what takes place. When work is done by an expanding gas, heat is always consumed. Indeed, a gas can be made to cool itself very considerably by simply allowing it to expand and do work. We have then a qualitative relation between heat and work. This qualitative relation was pointed out in 1841 by Julius Robert Mayer, and this marks the beginning of the mechanical theory of heat. Mayer went much farther than the merely qualitative stage, and made it probable that the amount of heat consumed in compressing a gas was exactly equivalent to the amount of work done. He thus showed that heat and work are of similar nature, and that *force*, or what we now call *energy*, is as indestructible as matter.

If heat and work are equivalent, and if the disappearance of a definite amount of heat means the production of a fixed amount of work, it still remains to determine the relation between the two — to determine the *mechanical equivalent of heat.*

The mechanical equivalent of heat was determined with unusual accuracy, for the time when the experiment was carried out, by Joule. He converted a known amount of work into heat by friction, and measured the amount of heat produced. According to Rowland the amount of heat required to raise one gram of water from zero to one degree is equivalent to about 42,550 gram-centimetres of work.

We have now expressed, in the mechanical equivalent of heat, the quantitative relation between heat and work.

Ratio between the Specific Heats calculated from the First Law of Thermodynamics. — It was shown by the combined labors of Mayer, Joule, Helmholtz, and others, that heat and all other forms of energy are indestructible, and also cannot be created. This is usually stated as the first law of thermodynamics. As this law denies the possibility of creating energy, it shows that the so-called perpetual motion of the first class, which would depend upon the creation of energy, is impossible.

The relation between the specific heat of a gas at constant pressure and the specific heat at constant volume, can be calculated at once from the first law of thermodynamics.

If we have a substance containing E amount of energy and we add $d\theta$ amount of heat, the change in the energy of the body, dE, will be equal to the amount of heat added, if no external work is done. If dW external work is done, we would have the following relation: —

$$d\theta = dE + dW. \qquad (1)$$

But the external work, dW, is equal to the pressure, p, times the change in volume dv, supposing the pressure to remain constant: —

$$d\theta = dE + pdv. \qquad (2)$$

The energy, E, will be dealt with as a function of the temperature and volume —

$$dE = \frac{\partial E}{\partial T}dT + \frac{\partial E}{\partial v}dv.$$

The last member of this equation, the change in energy with the change in volume, $\frac{\partial E}{\partial v}dv$, is equal to zero for gases; since the inner energy of a gas does not change with change in volume, when no external work is done. Equation (2) becomes then —

$$d\theta = \frac{dE}{dT}dT + pdv. \qquad (3)$$

If the volume is constant, $dv = 0$. $\because \frac{d\theta}{dT} = \frac{dE}{dT}$. The term $\frac{dE}{dT}$ is the specific heat of the gas at constant volume, which we will now call C_v.

If the pressure is constant, $\frac{d\theta}{dT} = C_v + p\frac{dv}{dT}$. But $\frac{d\theta}{dT}$ is the specific heat at constant pressure, C_p. Therefore, —

$$C_p = C_v + p\frac{dv}{dT}. \tag{4}$$

Returning to the general equation for gas-pressure, $pv = RT$, we see that if p is constant, $pdv = RdT$.

Substituting this value of pdv in equation (4), we obtain —

$$C_p = C_v + R. \tag{5}$$

The specific heat at constant pressure is equal to the specific heat at constant volume plus the gas-constant R.[1]

It only remains to determine the value of R in heat units in order to calculate the specific heat at constant volume from the specific heat at constant pressure. The equation $C_p - C_v = R$ shows that the work done in expanding under constant pressure, for a rise of one degree in temperature, is the same for all gases, since R is a constant for all gases. Let us deal with gram-molecular weights, and we can calculate the value of R very simply, since $R = \frac{p_0v_0}{273}$, as we have seen. A gram-molecular weight of a gas under a pressure of one atmosphere (76 cm. of Hg and at 0°) occupies a volume of 22,376 cc. Since the weight of an atmosphere is 1033.2 grams, we have —

$$R = \frac{22376 \times 1033.2}{273} = 84,685.$$

R is equal to 84,685 gram-centimetres of work. We know, however, that 42,550 gram-centimetres of work are equivalent to the amount of heat required to raise one gram of water from 0° to 1° C.—to one calorie. Therefore, —

$$R = 2 \text{ calories},$$

or more exactly, according to recent determinations of the mechanical equivalent of heat, to 1.99 calories. This applies to the molecular heats of gases. In case we are dealing with unit weights, we represent the specific heat at constant pressure by C_p and the specific heat at constant volume by C_v. The above equation for molecular heats becomes then —

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[1] For a fuller discussion see Ostwald: *Lehrb. d. allg. Chem.* I, 234.

$$C_p - C_v = \frac{2}{M},$$

where M is the molecular weight of the gas.

Returning to the molecular heats at constant pressure, it is necessary to subtract 2 from them to obtain the molecular heats at constant volume. The following table contains the molecular heats of a few gases at constant pressure and at constant volume. In the last column the ratio between the two is given.

	MOLECULAR HEAT AT CONSTANT PRESSURE, C_p	MOLECULAR HEAT AT CONSTANT VOLUME, C_v	$\frac{C_p}{C_v}$ RATIO
Oxygen	6.96	4.96	1.40
Nitrogen	6.83	4.83	1.41
Hydrogen	6.82	4.82	1.41
Chlorine	8.58	6.58	1.30
Bromine	8.88	6.88	1.29
Hydrochloric acid	6.68	4.68	1.43
Carbon dioxide	9.55	7.55	1.26
Sulphur dioxide	9.88	7.88	1.25
Carbon bisulphide	11.93	9.93	1.20
Ethylene	11.31	9.31	1.21
Methyl alcohol	14.66	12.66	1.16
Chloroform	18.71	16.71	1.12
Ethyl bromide	19.66	17.66	1.11
Ethylene chloride	22.67	20.67	1.10
Acetone	23.92	21.92	1.09
Stannic chloride	24.39	22.19	1.09
Ether	35.50	33.50	1.06
Oil of turpentine	68.80	66.80	1.03

The last column in this table contains the most interesting results. The ratio between the specific heats is not a constant, as could be foreseen from the method of calculating the specific heat at constant volume from the specific heat at constant pressure. The ratio necessarily decreases as the specific heats of the substances increase.

It should be noted that the specific heats of compounds are, in general, higher than the specific heats of the elements; and, further, that the compounds with a large number of atoms in the molecule have a greater specific heat than those with a smaller number. There are exceptions to these statements, but they are in general true.

The specific heat at constant volume is thus calculated from the specific heat at constant pressure, and the ratio of the two ascertained in this way. It is a matter of importance to determine the ratio between the two specific heats directly by experiment. This has been successfully accomplished.

Determination of the Relation between the Specific Heats of a Gas. — A number of methods have been suggested and used to determine the ratio of the two specific heats of a gas, but of these only one — the best and most convenient of them all — will be considered. Reference[1] is, however, given to other modes of procedure.

Dulong[2] first employed the velocity of sound in the gas to determine the ratio between its specific heats.

Instead of measuring the velocity of sound in the gas directly, Kundt[3] measures the wave-lengths, which are proportional to the velocity. A glass rod, with one end terminating in a glass tube filled with the gas to be investigated, is rubbed along its length. The gas in the tube is thus thrown into vibrations, and it remains to measure the wave-lengths of these vibrations. For this purpose some light powder, say lycopodium or finely divided cork, is added to the tube. The powder moves from the points of disturbance to the points of rest in the gas — from the loops to the nodes. It is then only necessary to measure the distance between two loops or two nodes to ascertain the length of the wave in the gas. Since the velocity of the sound is proportional to the wave-length, we know at once the velocity of the sound in the gas.

The ratio between the specific heats of any gas is determined at once from the relative lengths between the nodes in the gas in question and in air, knowing the ratio for air. Let M be the molecular weight of the gas, l_1 and l_2 the distance between two nodes in the gas and in air under the same conditions; and the ratio between the specific heats of air is 1.4. The ratio between the specific heats of the gas K is obtained thus: —

$$K = 1.4\,\frac{M l_1^2}{28.88\, l_2^2}.$$

The ratio between the specific heats of a gas, determined by the acoustical method, agrees very closely with that calculated from the first law of thermodynamics for a large number of gases. By examining the table of results on page 69, it will be seen that the ratio between the two specific heats — the one determined, the other calculated — does not exceed 1.43.

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[1] Laplace: *Mécan. Céleste.* V, 223. Assmann: *Pogg. Ann.* **85**, 1 (1852). Müller: *Wied. Ann.* **18**, 94 (1883).

[2] *Ann. Chim. Phys.* [2], **41**, 113 (1829). *Pogg. Ann.* **16**, 438 (1829).

[3] *Pogg. Ann.* **127**, 497 (1866); **135**, 337, and 527 (1868).

The direct determination of the ratio between the two specific heats in the case of mercury[1] gives a considerably higher value. And the same applies to argon and helium, as will be seen below: —

	Molecular Heat at Constant Pressure, C_p	Molecular Heat at Constant Volume, C_v	Ratio $\frac{C_p}{C_v}$
Mercury	——	——	1.66
Argon	——	——	1.66
Helium	——	——	1.66

The ratio between the specific heats in each of the above cases is not only higher than the ratio for many other gases, as previously calculated, but the surprising fact comes out that the ratio is the same for all three elements. What can this mean? It can scarcely be an accidental agreement.

We shall now see that, on the contrary, it is a very important fact and has a profound significance, throwing much light on the inner nature of the molecule itself.

Ratio between the Specific Heats of a Gas deduced from the Kinetic Theory. — The ratio between the specific heats of a gas can be calculated from the kinetic theory of gases.[2] We have already seen that the difference between the molecular heat at constant pressure and at constant volume is equal to the gas-constant R, and that R is equal to $\frac{pv}{273}$: —

$$C_p - C_v = \frac{pv}{273}.$$

It has been shown from the kinetic theory of gases that the pressure times the volume is equal to two-thirds the kinetic energy of the gas: —

$$pv = \frac{2}{3} K.$$

Therefore,

$$C_p - C_v = \frac{1}{273} \cdot \frac{2}{3} K. \qquad (1)$$

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[1] Kundt and Warburg: *Pogg. Ann.* **157**, 353 (1876).

[2] For a fuller discussion see Ostwald: *Lehrb. d. allg. Chem.* I, 251.

The entire energy in the gas (E) is the heat required to warm it from absolute zero to the temperature in question at constant volume. This is increased by the heat required to warm the gas from 0° to 1° by $\frac{1}{273}$ of E. But the heat required to warm the gas from 0° to 1° at constant volume is the specific heat at constant volume C_v. Therefore, $C_v = \frac{1}{273} E$. Dividing this value of C_v into equation (1), we have —

$$\frac{C_p - C_v}{C_v} = \frac{2}{3} \frac{K}{E};$$

$$\frac{K}{E} = \frac{3}{2}\left(\frac{C_p - C_v}{C_v}\right). \tag{2}$$

In case the total energy in the gas is the kinetic energy of the molecules, $K = E$, and we would have —

$$\frac{C_p - C_v}{C_v} = \frac{2}{3}; \text{ or}$$

$$\frac{C_p}{C_v} = \frac{5}{3} = 1.666.$$

This ratio (1.666) between the specific heats is calculated on the assumption that the total energy in the gas is kinetic, or that there is no intramolecular energy. This value of the ratio is, therefore, a maximum value. If we examine the ratios between the specific heats of elementary gases already given, either as determined directly by the acoustical method or as calculated, we shall find that in most cases the ratio is less than 1.666, and in no case does it exceed this value. Yet this value is reached with mercury, argon, and helium.

This raises the question why is the ratio found experimentally less in most cases than that calculated above, and why is the calculated value realized in a few cases? This question has apparently been answered quite satisfactorily.

In order that the entire energy in the gas should be kinetic, it is necessary that the molecules of the gas should be made up of one atom each. If there was more than one atom in the molecule, there would be intramolecular movement, and the total energy in the gas would not be the kinetic energy due to the movements of the molecules as a whole, but this quantity plus the intramolecular energy of the gas. If there was more than one atom in the molecule, K would not be equal to E, but less than E. Therefore $\frac{C_p - C_v}{C_v}$ would not be equal to two-thirds, but less than this quantity. Consequently $\frac{C_p}{C_v} < 1.666$.

This is exactly what we find in most elementary gases. The ratio of the two specific heats is less than 1.666, and we would conclude that these gases contain more than one atom in the molecule. We will recall that the molecular weights of most of the elementary gases, as determined by the densities of their vapors, showed that there was more than one atom in the molecule.

The conclusion in reference to mercury, argon, and helium is evident from what was stated above. Their molecules contain one atom each, or the molecule and atom are identical.

The conclusion that the ratio between the specific heats of a gas being 1.666 points to monatomic molecules has been called in question by some physicists, on purely physical grounds. A number of points have been raised, but perhaps the most important objection has been based upon the comparatively complex spectrum shown even by mercury vapor, which is monatomic in terms of the specific heat ratio. This element shows a number of lines in the spectrum, and it has been claimed that no monatomic molecule could give out so many wave-lengths of light.

While it is evident that this objection applies if the ultimate atom were meant, its force is not so clear if we recall that what we mean by the chemical atom is simply that unit of matter which we have not thus far been able to break down or subdivide. Indeed, as we have seen, the most probable theory as to the ultimate nature of matter states that what we must regard as the chemical atom must be enormously complex, and in all probability the atoms of what to us are different elements are simply complexes of the same ultimate "corpuscles."

Whatever weight we are inclined to attach to these objections from the physical side, we must not forget that in those cases where the ratio between the specific heats points to monatomic molecules, the vapor-density method also shows that the molecule and atom are identical. This has been verified in a manner which can leave no doubt in the case of mercury, and it is almost certain that the same result would be obtained with argon and helium.

The Second Law of Thermodynamics. — The calculation of the specific heat of a gas at constant volume from the specific heat at constant pressure involves, as we have seen, the first law of thermodynamics. For the sake of future reference this section should not be closed without a brief reference to the second law of thermodynamics.

The first law of thermodynamics states that it is impossible to create energy, and, therefore, perpetual motion of the first class is impossible. We might, however, conceive of a machine which could convert into mechanical work the heat of surrounding objects at the same temperature as itself. This would evidently be a perpetual motion; but since it differs from the first kind, it has been called perpetual motion of the second kind. The second law of thermodynamics states that perpetual motion of the second kind is impossible. In a word, heat cannot flow from a colder to a warmer body.

Given a gas of volume v and allow it to expand at constant temperature to a volume v_1. The maximum amount of work obtainable from this process is exactly equal to the work required to compress the same amount of gas from volume v_1 to volume v at constant temperature. This can easily be determined. If we are dealing with a gram-molecular weight of a gas with a volume v_1 and compress it to a volume v, the pressure being p, the work done is —

$$\int_v^{v_1} pdv.$$

Since $pv = RT$, the work done, W, is expressed thus: —

$$\begin{aligned} W &= \int_v^{v_1} pdv \\ &= RT\int_v^{v_1} \frac{dv}{v} \\ &= RT ln \frac{v_1}{v}. \end{aligned}$$

The maximum amount of work obtainable from a gram-molecular weight of a gas expanding from a volume v to a volume v_1 is given by the above equation, since this is equal to the work required to compress the gas under the same conditions from the volume v_1 to volume v. On examining this equation we see that the maximum amount of work obtainable depends only on the relation between the original and final volumes of the gas, and is independent of the absolute values of either. Frequent applications of this deduction will be made, especially in the chapter on electrochemistry.

THE SPECTRA OF GASES

Emission Spectra of Gases. — When a gas is heated to a sufficiently high temperature, it sends out light of definite wave-lengths. These wave-lengths were recognized by Kirchhoff and Bunsen[1] to be dependent upon the chemical nature of the gas, and to be characteristic of it. Upon this fact is based a method of chemical analysis, which has proved to be one of the most convenient and fruitful in the whole field of chemistry. It is only necessary to pass the light from a highly heated gas through a prism, or throw it upon a grating, when it will be refracted or diffracted, and the lines characteristic of the gas will appear. In this way it is possible to detect the presence of most of the chemical elements. If the element is a solid or liquid, it is only necessary to convert it into a gas to obtain its characteristic lines. This is easily accomplished if the boiling-point of the element is not too high. Those elements which boil only at very high temperatures are converted into vapor between the carbon poles of an electric arc, and then their spectra examined.

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[1] *Pogg. Ann.* **110**, 160 (1860); **113**, 337 (1861).

By means of spectrum analysis, then, the lines which are characteristic of the elements can be studied, and their wave-lengths determined. Having mapped out the lines which are characteristic of all the known elements, we are in a position to detect the presence of any new element. If when we examine the spectrum of a substance a line appears which can be shown not to belong to any known element, we conclude that we are dealing with a new substance, and then proceed to separate it and purify it by chemical methods. As is well known, many of our chemical elements were discovered by means of spectrum analysis. We need mention only cæsium, rubidium, thallium, indium, and gallium, and quite recently the spectroscope has proved of incalculable service in the discovery of the new substances in the atmosphere, by Ramsay. Spectrum analysis has now reached such a high degree of perfection, due especially to the concave grating designed by Rowland,[1] that it is certainly the most sensitive means at our disposal for detecting small traces of substances. In examining any substance to-day for unknown elements, or in testing any element in which some foreign material is suspected, resort is always had, whenever possible, to the spectroscope.

Absorption Spectra of Gases; Law of Kirchhoff.—If white light is passed through a gas and then through a prism or thrown upon a grating, it is seen to contain dark lines exactly in the places occupied by the bright lines of the gas. Kirchhoff recognized this fact and announced his law: *A gas absorbs exactly the same wave-lengths of light as, under the same conditions, it can itself emit.* This discovery was of great importance as throwing light on a class of phenomena up to that time not understood. Fraunhofer had early discovered that when sunlight is refracted and separated into its colors the spectrum is not continuous, but is marked by a large number of dark lines. The law of Kirchhoff explained the presence of these dark lines. The light coming from the sun had passed through the vapors of certain elements, and the same wave-lengths which these gases could emit had been absorbed by them. If this is true, we have a means of determining at least some of the elements which exist in the sun. It is only necessary to find out with what characteristic bright lines of our terrestrial elements the dark lines in the solar spectrum correspond, in order to determine which of our elements are present in the sun. In this way a large number of the dark lines in the solar spectrum have been "identified," as it is stated; *i.e.* shown to have the same wave-lengths as the bright lines of known elements. We can now state that about half[1] of the known terrestrial elements certainly occur in the sun, and about eight of the remaining terrestrial elements may occur in the sun. Among the solar elements we find most of the metals which occur on the earth.

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[1] *Phil. Mag.* **16**, 197 (1883).

Spectrum analysis has not been content with determining the elements which occur in the sun, but an attempt has been made to determine the elements which occur in different parts of the sun. Work during the total eclipse of the sun, or by specially devised methods, has shown that the *chromosphere* always contains hydrogen, titanium, helium, and calcium, and frequently contains a large number of other elements, such as sodium, barium, iron, and magnesium. Similarly, the spectroscope has been applied to the *corona* during a total eclipse, but the composition of the corona is still in doubt.

The spectroscope has also been applied to the stars, planets, comets, moon, nebulæ, etc.; but for the results obtained reference only can be made to the excellent little book of Landauer, *Die Spectralanalyse.*

Relations between the Spectrum Lines of the Elements. — An element may give out light of a few wave-lengths, or of many. Some elements are represented by comparatively few lines in the spectrum, while others are represented by a large number — the lines of iron and uranium may number thousands. We will look first for *relations between the lines of the same element.* Since light is regarded as a wave-motion of the ether, the different spectrum lines correspond to different wave-lengths. It would seem probable that the different wave-lengths sent out by the same kind of atoms or molecules would bear some simple relation to one another. One naturally thinks of the wave-lengths of sound sent out by a vibrating string, and recalls the simple relations between them. Relations as simple as these have not been discovered in the case of light, but generalizations of value have been reached. The first attempt to point out relations between the wave-lengths of the vibrations sent out by the same element was made by Lecoq de Boisbaudran,[1] but the first successful attempt was made by Balmer.[2] He showed that the wave-lengths of the first spectrum of hydrogen can be accurately calculated from the equation —

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[1] Janssen: *Compt. rend.* **68**, 93. Lockyer: *Proc. Roy. Soc.* **17**, 91, 104, 128 (1868). Zöllner: *Pogg. Ann.* **138**, 32 (1869). Huggins: *Proc. Roy. Soc.* **17**, 302 (1868).

$$\lambda = A\frac{n^2}{n^2-4},$$

n having the values 3 to 15, and A the value 3647.20.

It was, however, Kayser and Runge,[3] who first deduced any general relation which obtained for a number of the elements. Their equation is —

$$\frac{1}{\lambda} = A + Bn^{-2} + Cn^{-4},$$

taking instead of the wave-length λ, its reciprocal. To test their formula they redetermined more accurately the wave-lengths of the lines of many of the elements, and pointed out the existence of distinct *series* of lines. In the spectra of the alkali metals they found three distinct series of lines. The first series, known as the Primary Series, occurring only with the alkalies, was very bright, containing some of the strongest lines in the whole spectrum, and had unequal differences in period. The First Subordinate Series was composed of very bright lines, but not so bright as the Primary Series, and the differences in period were equal. The Second Subordinate Series was composed of weaker lines, and the differences in period were equal.

The relations between the lines of other elements were not as well defined as with the alkalies. Certain elements showed the existence of secondary series, but, in general, as we pass farther and farther from the alkalies in the Periodic System, the relations between the lines of any element become less distinct. For further details in this connection reference must be had to the original papers.[1]

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[1] *Compt. rend.* **69**, 694.

[2] *Wied. Ann.* **25**, 80 (1885).

[3] *Abhandl. Berlin. Akad.* 1888, 1889, 1890, 1891, 1892, 1893. *Wied. Ann.* **52**, 114 (1894). *British Ass. Report*, 1888, p. 576. *Chem. Zeitg.* **16**, 533.

The relations between the spectrum lines of different elements are of greater interest, from the physical-chemical standpoint. Lecoq de Boisbaudran[2] thought he had discovered certain relations between the spectra of potassium, rubidium, and cæsium, and concluded that as the atomic weight increases, the spectra of the alkalies and alkaline earths tend more and more toward the red. This has since been shown by Ames[3] not to be strictly true in the case of magnesium, zinc, and cadmium.

The work of Kayser and Runge, and of Rydberg,[4] are again of chief importance in connection with the relations between the lines of different elements. Elements belonging to the same groups of the Mendeléeff Table have analogous spectra. It has already been pointed out that the primary series of lines appears only with the alkali metals. The first three groups of elements have been arranged in the following order with respect to relations between their spectra:[5]—

(1) Li, Na, K, Rh, Cs.
(2) Cu, Ag.
(3) Mg, Ca, Sr.
(4) Zn, Cd, Hg.
(5) Al, In, Th.

Within these groups the spectrum tends more and more toward the red, with increasing atomic weight. This is what we might expect, the heavier atom vibrating more slowly and sending out fewer waves in a given time. As we pass, however, from one group of these elements to another, the spectrum tends toward the violet, with increase in atomic weight. These relations must, of course, be regarded as only first approximations to any general truth, and when we consider that some elements vibrate in thousands of periods, or at least give thousands of lines in the spectrum, it will probably be a long time before any comprehensive generalization will be reached connecting anything like all the wave-lengths sent out by the different elements. That there are, however, fundamental relations between these wave-lengths no one can doubt.

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[1] Rydberg: *Compt. rend.* **110**, 394 (1890). *Ztschr. phys. Chem.* **5**, 227 (1890). *Wied. Ann.* **50**, 629 (1893); **52**, 119 (1894). Landauer: *Die Spectralanalyse*, p. 64.

[2] *Compt. rend.* **69**, 610.

[3] *Phil. Mag.* **30**, 33 (1890).

[4] *Loc. cit.*

[5] Landauer: *Die Spectralanalyse*, p. 69.

CHAPTER III

LIQUIDS

RELATIONS BETWEEN LIQUIDS AND GASES

General Properties of Liquids. — The properties of liquids as such are so different from the properties of gases that we would suspect little or no connection between these two states of aggregation. Liquids have their own definite volumes, which are only slightly changed by change in conditions. The volume of a liquid is slightly diminished by increase in pressure, and increased by rise in temperature; but the change in either case is small. According to Amagat,[1] the coefficient of compression of water varies from 0.000043 at comparatively low pressures to 0.000024 at pressures in the neighborhood of 3000 atmospheres. The compression coefficient of mercury is only about 0.0000032 for pressures of a few atmospheres.

The increase in the volume of water with increase in temperature is seen in the few results given in the following table, which is taken from the work of Volkmann.[2] The unit is water at + 4° C.

Expansion of Water

Temperature	Volume	Temperature	Volume
0°	1.000122	40°	1.00770
2°	1.000028	50°	1.01197
4°	1.000000	75°	1.02572
6°	1.000031	90°	1.03574
10°	1.000261	100°	1.04323
20°	1.001731		

Similarly, the expansion coefficient of mercury varies from 0.0001813 at 0° to 0.0001884 at 360°.

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[1] *Compt. rend.* **103**, 429 (1886); *Journ. de Phys.* [2], **8**, 197.

[2] *Wied. Ann.* **14**, 260 (1881).

If we recall that the volume of a gas decreases with the pressure according to the law of Boyle, and increases with the temperature according to the law of Gay-Lussac, we will see the marked difference between the persistency of the volume of a gas and that of a liquid.

The particles of a liquid move comparatively freely over one another, but the resistance to movement is much greater here than with gases. This is usually expressed by saying that the inner friction of liquids is greater than that of gases.

Liquids in general represent matter in a much more condensed form than gases. A given volume of a liquid when converted into a gas occupies many times its volume in the liquid state; but here, again, pressure must be taken into account, since the density of a gas can be greatly increased by pressure alone. These are some of the most striking differences between matter in the liquid and matter in the gaseous state.

If, however, we examine gases and liquids more closely, we shall see that the differences are mainly differences of degree — the state of aggregation depending chiefly upon temperature and pressure. That there are close relations between the gaseous and liquid states is clearly brought out by a study of the transformation of gases into liquids and of liquids into gases.

The Liquefaction of Gases. — The problem of the liquefaction of gases early attracted attention. It was very easy to liquefy some substances, while others remained in the gaseous state even at quite low temperatures. Van Helmont[1] distinguished between those substances which cannot be liquefied and those which can, by calling the former "gases" and the latter "vapors."

The first really important step in the liquefaction of gases which condense only at very low temperatures we owe to Faraday (1823). He heated chlorine hydrate in a glass tube, one end of which was kept cool, and obtained chlorine as a yellow liquid. This was followed[2] by the liquefaction of a number of other gases, such as sulphurous acid, hydrogen sulphide, carbonic acid, cyanogen, ammonia, etc. In these experiments, Faraday made use both of high pressure and low temperature, — the two conditions which underlie all subsequent work.

Bussy[3] worked at low temperatures, but did not use high pressures. He liquefied sulphurous acid, and made the important discovery that when this liquid was allowed to evaporate on the air, a

[1] Kopp: *Geschichte der Chemie*, I, p. 121.

[2] *Phil. Trans.* **113**, 189.

[3] *Ann. Chim. Phys.* [2], **26**, 63 (1824). *Pogg. Ann.* **1**, 237 (1824).

much lower temperature was produced. This, as we shall see, has proved to be of fundamental importance in connection with the liquefaction of the more resistant gases. Utilizing this fact, Bussy was able to liquefy chlorine and ammonia.

Carbon dioxide was liquefied in fairly large quantities by Thilorier[1] in 1834, by means of a new apparatus[2] which he devised for this purpose. He studied a number of the physical properties of liquid carbon dioxide,—its vapor pressure, solubility, etc.,—and then turned his attention to the production of low temperatures by allowing the liquid to volatilize. By means of a spray of liquid carbon dioxide low temperatures could be reached; but by mixing liquid carbon dioxide and liquid ether, powerful refrigerating effects could be produced. Thilorier not only liquefied, but succeeded in solidifying carbon dioxide. The liquid carbon dioxide was allowed to expand, when a part volatilized, and in doing so extracted enough heat from the remainder to convert it into a solid. When the solid carbon dioxide is mixed with ether, a powerful refrigerant is produced, which has proved to be of great service in obtaining comparatively low temperatures. Temperatures of from − 100° C. to − 110° C. can be produced by means of this mixture, which has come to be known as *Thilorier's Mixture.*

Faraday published the results of his second attempt to liquefy gases in 1845.[3] The incentive, as he says himself, was to obtain the so-called "permanent gases" in liquid or solid form. He worked with higher pressures than in his first experiments, and also used lower temperatures, now made possible by the discovery of Thilorier's mixture. A number of gases such as ethylene, hydrobromic acid, phosphine, etc., succumbed to this treatment, and were obtained as liquids. A number of gases were also solidified, such as hydriodic, sulphurous, and hydrobromic acids, ammonia, cyanogen, and nitrous oxide. Faraday did not succeed in liquefying hydrogen, oxygen, nitrogen, carbon monoxide, or nitric oxide.

Natterer[4] devised an apparatus for producing very high pressures, and then attempted to liquefy the so-called permanent gases — oxygen, hydrogen, etc.[5] He subjected these gases to higher and higher pressures, until finally a pressure of between three and four thousand atmospheres was used. At the same time he used the lowest temperature which he could obtain by mixing solid carbon dioxide and ether. He was unsuccessful, and the permanent gases still remained unliquefied.

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[1] *Ann. Chim. Phys.* [2], **60**, 427 (1835).

[2] *Lieb. Ann.* **30**, 122 (1839).

[3] *Phil. Trans.* **135**, 155 (1845).

[4] *Journ. prakt. Chem.* **35**, 169 (1845).

[5] *Wien. Ber.* **5**, 351 ; **6**, 557 and 570 ; **12**, 199.

During the next thirty years (1845–1875) not many gases were added to the list of those which had been liquefied. The so-called "permanent gases" had baffled all attempts to liquefy them, and still continued to do so. But during this period the nature of gases was studied more closely, and knowledge acquired which made possible the subsequent liquefaction of all gases.

Some of the results of the work of this period will be considered in more detail a little later. Suffice it to say here that it was shown that for every gas there is a temperature above which it cannot be liquefied, no matter how great the pressure to which it is subjected. This is called the *critical temperature* of the gas.

It soon became obvious, then, that every gas must be cooled down at least to its critical temperature, before it can be converted into a liquid by pressure. After this fact became clearly recognized, experimenters saw that they must look rather to the securing of low temperatures than of high pressures, in order to convert the "permanent gases" into liquids.

It was not until 1877 that Cailletet[1] succeeded in liquefying oxygen and carbon monoxide; and it was only a few weeks later that oxygen was also liquefied by Pictet.[2] The method employed by Cailletet consisted in subjecting the gas to a fairly high (300 atmospheres) pressure in a very simple apparatus,[3] cooling the gas down to a low temperature by means of liquid sulphurous acid, and then allowing the gas to suddenly expand by releasing the pressure. In addition to oxygen and carbon monoxide, Cailletet succeeded also in liquefying nitrogen and air, but the experiments with hydrogen were not as satisfactory, although it is stated that a mist was seen in the tube containing the hydrogen, when the pressure was removed. The experiments of Pictet[4] cannot be described in detail. He succeeded in liquefying oxygen, as has been stated, and probably hydrogen also, and, indeed, may have obtained a little solid hydrogen.

We now come to the very important and successful work of the Russians, Wroblewski and Olszewski.[5] Their method consists in subjecting the gas to be liquefied to considerable pressure, but at the same time cooling it down to a very low temperature. The low temperature is secured by causing a liquid with low boiling-point to boil under diminished pressure. Thus, in the liquefaction of oxygen a temperature of −130° was secured by boiling liquid ethylene under diminished pressure. The oxygen was then liquefied at a pressure not much above twenty atmospheres. Similarly, when nitrogen was cooled to a very low temperature, subjected to a pressure of 150 atmospheres, and part of the pressure released, it was obtained as a liquid.

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[1] *Compt. rend.* **85**, 1217 (1877). [2] *Ibid.* **85**, 1214, 1220 (1877).

[3] *Ann. Chim. Phys.* [5], **15**, 132 (1878).

[4] *Ibid.* [5], **13**, 145 (1878).

[5] *Wied. Ann.* **20**, 243 (1883).

In 1884 Wroblewski[1] liquefied hydrogen, using liquid oxygen under diminished pressure as the refrigerating agent. He assigued the following boiling-points to four of the more common gases:—

	PRESSURE	BOILING-POINT
Oxygen	1 atmosphere	−184°.0 C.
Nitrogen	1 atmosphere	−194°.3 C.
Air	1 atmosphere	−192°.2 C.
Carbon Monoxide . .	1 atmosphere	−186°.0 C.

When these liquids were boiled under diminished pressure, a temperature somewhat lower than −200° C. could be obtained. Olszewski made use of the low temperature obtained in this way to liquefy hydrogen.[2] The gas was subjected to a pressure of nearly two hundred atmospheres, and cooled as low as possible by boiling oxygen under a pressure of a few millimetres of mercury. He was not able to obtain any quantity of liquid hydrogen.

Olszewski solidified a number of the very low-boiling liquids. Liquid carbon monoxide,[3] which boiled at −190°, was evaporated under diminished pressure. The temperature sank to −211°, and a part of the liquid solidified. Nitrogen[4] was solidified in a similar manner at a temperature of −214°. Solid nitrogen, when boiled under diminished pressure, produced a temperature of −225°. Liquid air evaporated under low pressure gave −220°. Olszewski found the boiling-point of oxygen to be −181°.4, of nitrogen −194°.4, and of carbon monoxide −190°. In 1891 he made another attempt to liquefy hydrogen,[5] using liquid air and liquid oxygen as the refrigerants. While not successful to any marked extent, he was able to fix the boiling-point of hydrogen at about −243°.5.

[1] *Compt. rend.* **98**, 149 (1884).

[2] *Ibid.* **98**, 365, 913 (1884).

[3] *Ibid.* **99**, 706 (1884).

[4] *Ibid.* **100**, 350 (1885).

[5] *Phil. Mag.* [5], **39**, 188 (1895).

The experiments of Dewar[1] contributed much to our knowledge of low-boiling liquids. He devised an apparatus[2] for liquefying such gases as oxygen, nitrogen, etc., on a comparatively large scale, and in 1893 solidified air.[3] Dewar greatly facilitated the work with these low-boiling liquids, by devising double-walled bulbs and test-tubes,[4] and pumping out the air between the two walls. In this "vacuum-jacketed" apparatus these liquids evaporate comparatively slowly and could be preserved for a relatively long time.

At this time the problem of liquefying gases was solved by a new method, which made it possible to liquefy such gases as the air on a commercial scale. Hitherto, the gas had been cooled chiefly by evaporating some low-boiling liquid under diminished pressure, but plainly this was not economical. The final cooling of the gas was effected by allowing it to expand. The methods of liquefying air used by *Linde, and also by Hampson and Tripler, are apparently based upon essentially the same principle.* The gas is compressed, and the heat which is liberated removed. The gas is then allowed to expand, usually through a small opening, and thus its temperature lowered. This cold gas is then allowed to cool more of the compressed gas, and finally some of the latter is obtained in liquid form.

Quite recently some extremely interesting results have been obtained in connection with the liquefaction of the most resistent gases. Argon was liquefied by Olszewski[5] in 1895, using liquid oxygen as the refrigerating agent. It boiled at – 187° and froze at – 191°. He also attempted to liquefy helium,[6] using at first liquid oxygen, and then liquid air, as the refrigerating agents. Although a temperature of – 220° was obtained with liquid air, under diminished pressure, the helium did not liquefy under a pressure of 140 atmospheres.

Fluorine was liquefied by Moisson and Dewar[7] in 1897. This is, of course, a remarkable experiment, when we think of the chemical nature of fluorine. The fluorine was cooled to –190° by means of liquid air, liquefied, and received in a glass bulb. Fluorine boils at –187°, and at this low temperature loses much of its chemical activity. It does not act upon iron, and does not replace iodine from its compounds. The liquid fluorine was cooled to –210° without solidifying. Fluorine has, however, been recently[8] solidified.

[1] *Phil. Mag.* **18**, 210 (1884).

[3] *Chem. News*, **67**, 126 (1893).

[2] *Proc. Roy. Inst.* 1886, 550.

[4] *Proc. Roy. Inst.* **14**, 1 (1896).

[5] *Trans. Roy. Soc.* **186**, 253 (1895). Communicated by Ramsay.

[6] *Wied. Ann.* **59**, 184 (1896). *Nature*, **54**, 377 (1896).

[7] *Compt. rend.* **124**, 1202 (1897) ; **125**, 505 (1897).

[8] *Nature*, March 26th, 1903, 497.

The problem of liquefying hydrogen in any appreciable quantity was solved by Dewar[1] in 1898. A mixture of liquid nitrogen and hydrogen was used to cool down the gas. Under diminished pressure this would give a temperature of at least −205°. Hydrogen gas cooled to this temperature, and under a pressure of about 180 atmospheres, was allowed to flow through a fine opening into a "vacuum-jacketed" vessel, kept below −200°. Hydrogen liquefied under these conditions at the rate of some four or five cubic centimetres of liquid per minute. The boiling-point of liquid hydrogen, as determined by the platinum thermometer, is −238°. This has since been redetermined by a platinum-rhodium thermometer, and found to be −246°.

Dewar[2] has also succeeded in liquefying helium by placing a tube containing this gas in liquid hydrogen, and, finally, has obtained hydrogen in the solid form.[3] He attempted to solidify hydrogen by placing some of the liquid in a tube surrounded by liquid hydrogen in a vacuum-jacketed vessel, and boiling the hydrogen in the outer vessel under diminished pressure. This experiment was not successful. The hydrogen in the inner vessel may have been cooled below its freezing-point, but remained undercooled and did not solidify. However, by means of a simple apparatus in which the refrigerating effect of evaporation under diminished pressure could be better realized, Dewar obtained hydrogen in the solid form. The melting-point of hydrogen must be about −255°, and a slightly lower temperature can be obtained by evaporating solid hydrogen.[4]

We see, then, from the above, that all known gases have been liquefied, and all, with the exception of helium, have been solidified. The relation between the gaseous and liquid state is evidently a very close one — the state of aggregation which obtains depending obviously upon temperature and pressure, but chiefly upon temperature. A further point of very great interest comes out in connection with the liquefaction of the more permanent gases. We are able to realize experimentally a temperature which is but slightly above the absolute zero. That many important discoveries will be made by working in this region of extreme cold is almost certain, now that we have refrigerating agents of such intensity and in such quantity at hand.

In tracing the development of the principles and methods involved in liquefying gases, it was pointed out that there is a temperature for every gas, above which it cannot be liquefied by pressure. This and certain analogous constants for gases must be studied more closely.

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[1] *Proc. Roy. Soc.* **63**, 256 (1898). [2] *Ibid.* **63**, 257 (1898).

[3] *Chem. News*, **80**, 132 (1899).

[4] For details in connection with the liquefaction of gases, see the admirable little book by Hardin, *Liquefaction of Gases.*

Critical Temperature and Critical Pressure. — Cagnaird de la Tour[1] observed in 1822 that ether and alcohol pass completely into vapor in a very small space, when the temperature is above a certain point. Also, that two volumes of ether volatilize at the same temperature as one volume into the same space. This made it probable that there was a temperature above which these liquids could not remain in the liquid state, but would pass over into vapor regardless of the pressure. This observation made but little impression, until Andrews[2] showed much later (1869) that there is a temperature for every gas, above which it cannot be liquefied. This temperature was called by Andrews the *Critical Temperature* of the gas. The work of Andrews was done largely with carbon dioxide. When the tube containing this gas was brought to a temperature of 13°.1, and the gas subjected to a pressure of 48.9 atmospheres, a liquid began to appear, and the volume of the gas continued to diminish without any considerable increase in pressure being required. At 21°.5 similar results were obtained. At somewhat higher temperatures, however (31°.1 and 32°.5), results of a very different character manifested themselves. Although there was a marked decrease in volume at a certain definite pressure, yet no liquid separated. There was no evidence that any liquid had been formed. At still higher temperatures the abrupt-

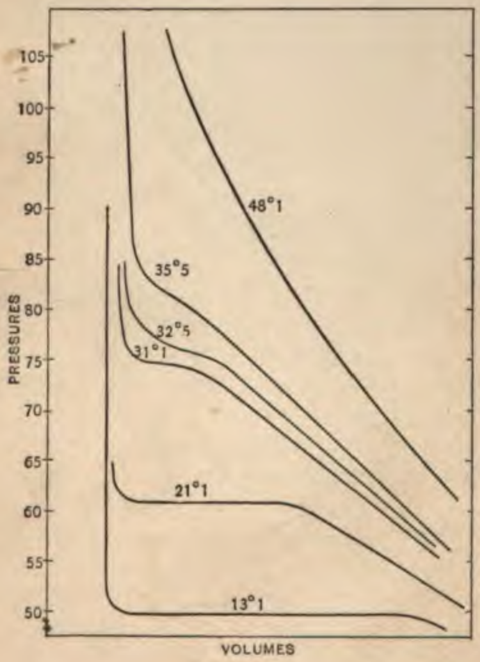

Fig. 10.

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[1] *Ann. Chim. Phys.* **21**, 127, 178 (1822); **22**, 410 (1823).

[2] *Trans. Roy. Soc.* 1869 [2], 575.

ness of change in volume at any definite pressure became less and less, and entirely disappeared at 48°.1. These results are seen best by plotting them in curves; the abscissas are volumes, the ordinates pressures.

The curve for 13°.1 shows that when a pressure of nearly 50 atmospheres is reached, the volume diminishes very greatly without any marked increase in pressure. This means that the gas has passed over into liquid at this pressure. The curve for 21°.1 is similar to the lower curve. An abrupt transition from gas to liquid takes place, but at a higher pressure. The curves for 31°.1, 32°.5, and 35°.5 show less and less abruptness, but at none of these temperatures is any liquid produced. The curve at 48°.1 shows no break, being perfectly smooth throughout. The temperature above which carbon dioxide cannot be liquefied was found by Andrews to be 30°.92, and this is, therefore, the critical temperature of the gas.

The temperature above which a gas cannot be liquefied has been termed by Mendeléeff[1] the **absolute boiling-point of the gas**. This is obviously the same as Andrews' critical temperature.

The pressure which will just liquefy the gas at the critical temperature has been termed the **critical pressure**. The substance has a certain definite density under these conditions, and this is its **critical density**. The reciprocal of the critical density is the **critical volume**.

Many of the critical constants of liquids will be found in a paper by Heilborn,[2] but since some of these have been quite recently determined with greater accuracy, the original papers bearing upon the liquefaction of gases and the properties of the liquids formed must be consulted. The critical temperatures and pressures of some well-known liquids are given in the following table: —

	Critical Temperature	Critical Pressure
Hydrogen	− 225°.0	15.0 atmospheres
Nitrogen	− 146°.0	35.0 atmospheres
Carbon monoxide	− 141°.0	36.0 atmospheres
Argon	− 120°.0	40.0 atmospheres
Fluorine	− 121°.0	50.6 atmospheres
Oxygen	− 118°.8	50.8 atmospheres
Methane	− 95°.5	50.0 atmospheres
Carbon dioxide	− 31°.0	75.0 atmospheres
Ammonia	− 130°.0	115.0 atmospheres
Chlorine	− 144°.0	83.9 atmospheres
Bromine	− 302°.2	

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[1] *Lieb. Ann.* **119**, 1 (1861).

[2] *Ztschr. phys. Chem.* **7**, 601 (1891).

The examples given in this table show the great differences in the critical temperatures of different liquids. It also shows that the critical pressures of liquids are, in general, not high. If the temperature of the gas is below the critical temperature, the pressure required to liquefy the gas is below the critical pressure. In the liquefaction of gases, then, low temperature is far more important than high pressure. Indeed, the temperature must be at least down to the critical temperature. If the temperature is still lower, very slight pressure may liquefy the gas. We can now see why the earlier experimenters were not successful when they tried to liquefy such gases as oxygen, nitrogen, hydrogen, etc. They used in some cases enormous pressures amounting to thousands of atmospheres; but did not cool the gases down to the critical temperatures. After these gases were sufficiently cooled they were liquefied at moderate pressures.

Continuity of Passage from the Liquid to the Gaseous State. — It will be seen from what has been said in reference to critical temperature and pressure, that a liquid can be transformed into vapor without becoming heterogeneous at any time. If the liquid is warmed above its critical temperature, a pressure is produced which is greater than the critical pressure. The volume may now be increased to any extent, yet the substance which was originally liquid remains homogeneous. The passage from the liquid to the gas is thus perfectly continuous, and it is impossible to say where the liquid state ends and the gaseous begins. The condition of matter at and near the critical point has always perplexed men of science, and many opinions have been expressed concerning it. Andrews discussed this condition in connection with carbonic acid. He pointed out that if this gas above the critical temperature is subjected to a pressure considerably above the critical pressure, there is an enormous decrease in volume. The carbon dioxide under this condition is neither gas nor liquid, but occupies a position between the two.

Certain phenomena manifested by substances around the critical point have been very carefully studied. Clark[1] showed that the density of the vapor was equal to that of the liquid at the critical point. This has been defined as the *critical density*. The critical point is, then, that at which the density of vapor and liquid are equal. Ramsay[2] concluded from the experiments of others and from his own that the liquid state may persist beyond the critical point, and this opinion is shared by other experimenters.[1] Hannay,[2] on the contrary, is of the opinion from his own work, that the critical point marks the limit of the liquid condition, and suggests the term "vapor" for matter just above the critical point. It, however, seems best to still limit the states of matter to three,—gas, liquid, and solid,—as Hardin points out.[3] Defining gas as we do, as having neither any definite form nor occupying any fixed volume, but capable of nearly indefinite expansion, it is obvious that a substance above the critical point is in the gaseous condition.

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[1] *Proc. Phys. Soc.* **4**, 41.

[2] *Proc. Roy. Soc.* **31**, 194 (1881).

Just as a liquid can be transformed into a gas without any break in continuity, so can a gas be transformed into a liquid by a continuous process. The gaseous and liquid states, then, approach as the critical point is reached, and either can be made to pass into the other without any breach in continuity.

The Kinetic Theory of Liquids.—The close relation which we have just seen to exist between liquids and gases has led to the application of the kinetic theory of gases also to liquids. Since the passage from a liquid to a gas, and *vice versa*, under certain conditions is so gradual that we cannot say where the one state of aggregation ends and the other begins, it is highly probable that any theory which obtains for the one state would apply, to some extent at least, to the other.

The liquid state, as we have seen, represents matter in a much more concentrated condition than the gaseous state. There is a much larger number of molecules in a given volume of a liquid, and consequently the collisions between the moving molecules are much more frequent. There would thus result in the liquid an enormous pressure, were it not for the attractive forces between the molecules. These attractive forces hold the molecules together and prevent them from flying off with explosive violence. Only those molecules which approach the surface of the liquid with unusually great velocity can so far escape from the attractions of the other liquid molecules as to fly off into the space above the liquid. This explains the existence of vapor above every liquid. We know, however, that if these molecules fly off into a closed space above the liquid, the vapor-pressure thus produced cannot exceed a certain limit at any given temperature. We can clearly see the reason for this in terms of our theory. The molecules of the vapor, in their movements through the confining space, come in contact with the surface of the liquid. Some of these are continually coming within the range of the attractive forces of the liquid molecules, and are drawn down, as it were, into the liquid again. There is thus a continual exchange going on between the liquid and the vapor, some liquid particles passing off as vapor, and some vapor particles condensing as liquid, until a condition of equilibrium is reached. Equilibrium is established when the vapor-pressure has reached such a point that the same number of gaseous molecules are condensed in any unit of time as there are liquid molecules converted into vapor. We have seen that it is only the molecules with the greatest kinetic energy which can so far overcome the molecular attractions as to escape from the liquid as vapor, and this of course lowers the mean kinetic energy of the liquid. We know that when a liquid evaporates, the mean kinetic energy of the liquid molecules decreases, or, as we say, the temperature is lowered. If the liquid is in such a position that it can absorb heat, it does so; and the heat required to effect complete vaporization of a liquid is very great. This explains why the vapor-tension of a liquid is increased with rise in temperature. The addition of heat increases the kinetic energy of the liquid molecules, and more are capable of overcoming the molecular attractions and flying off as vapor in a given unit of time. The number of molecules in the condition of vapor is therefore greater, and the vapor-pressure is greater the higher the temperature.

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[1] Jamin: *Phil. Mag.* [5], **16**, 75 (1883). Cailletet and Colardeau: *Ann. Chim. Phys.* [6], **18**, 269 (1889).

[2] *Proc. Roy. Soc.* **30**, 478 (1880).

[3] *Liquefaction of Gases*, p. 95.

So much for the qualitative application of the kinetic theory of gases to liquids. The quantitative application will be made by attempting to apply the equation of Van der Waals for gases also to the continuous passage from the gaseous to the liquid condition.

Van der Waals' Equation applied to the Continuous Passage from the Gaseous to the Liquid Condition. — The equation of Van der Waals for gases, it will be remembered, is: —

$$\left(p+\frac{a}{v^2}\right)\left(v-b\right)=RT.$$

When this is arranged with respect to the powers of v, we have: —

$$v^3-v^2\left(\frac{RT}{p}+b\right)+v\frac{a}{p}-\frac{ab}{p}=0.$$

This equation has three solutions, being a cubic equation, which means that there are three values of v for any given value of p. We can understand the significance of two volumes for one pressure, the one that of the liquid, the other that of the vapor; but of the third we know nothing. If we construct the curve corresponding to the above equation, we will have the following figure (Fig. 11). The abscissas represent volumes, and the ordinates pressures. Each is an isothermal curve, and the temperature increases from curve 1 to curve 6. Curve 1 represents a temperature below the critical temperature, and curve 6 is above the critical temperature. If we follow one of these isothermals, say 1, we find that as the pressure increases from A to C, the volume continually decreases; but as the pressure decreases from C to E, the volume still continues to decrease. As the pressure increases again from E, the volume continues to decrease.

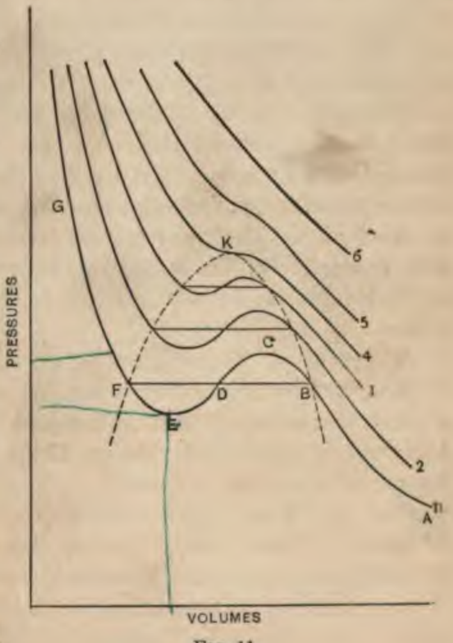

Fig. 11.

If we compare this curve with the results of experiment, — say Andrews' work with carbon dioxide, — we find that the first part of curve 1 corresponds to the results obtained. When gaseous carbon dioxide was subjected to increasing pressure, the volume decreased as represented by the curve AB. Since the temperature is below the critical, when a certain pressure was reached, represented by the point B, the gas liquefied. The volume thus changed very rapidly without any change in pressure, until a volume corresponding to that of the liquid was reached. This is represented by the straight line BF. With further increase in pressure beyond the point F there was very slight diminution in volume, since the volume of a liquid is only slightly changed with large changes in pressure.

The portion of the curve which cannot be verified experimentally is that represented by *BCDEF*. The temperature here is below the critical, and when a certain pressure is reached there is an abrupt transition from the gas to the liquid. The substance at this volume is heterogeneous, *i.e.* part gas and part vapor. Since the equation of Van der Waals applies only to homogeneous conditions, — to a continuous transformation from one state of aggregation to the other, — it is obvious that it cannot apply to this condition. It is possible to follow the curve a little beyond *B* by studying a supersaturated vapor, and to proceed a short way from *F* toward *E* by studying a superheated liquid, but it is impossible to proceed to any considerable distance because of the instability of these states.

If we now examine curves 2, 3, etc., corresponding to increasing temperatures, we find that the three volumes corresponding to a given pressure more and more nearly coincide. The middle portion of the curve deviates less and less from the straight line, until in 4 we have the three volumes absolutely coinciding. The physical significance of this point, where the three volumes become equal, is very interesting. It is the point where the volume of the gas is equal to that of the liquid, or where there is no discontinuity between the two states. It is only at this point that gas and liquid can be transformed into one another isothermally and without loss in continuity. The temperature, pressure, and volume at this point are, respectively, the critical temperature, critical pressure, and critical volume. In a word, this is the **Critical Point** of the substance.

The method of obtaining this point is evident from Fig. 11. It is only necessary to draw a number of isothermal curves for constant values of a and b in the Van der Waals equation, starting at a temperature considerably below the critical temperature. As the temperature of the isothermal approaches the critical temperature, the values for the three volumes approach one another and finally become equal when the isothermal corresponding to the critical temperature is reached. We can thus determine the point *K* from the constants in Van der Waals' equation, which is the same as to say that we can determine the critical temperature, critical pressure, and critical volume of a substance.

In concluding this section attention should be called again to the fact that the application of Van der Waals' equation to liquids has been only partially successful. While it has shown relations between properties as different as the deviations from the ordinary gas laws and the critical constants, yet there are many and quite appreciable differences between the values as calculated by means of this equation and as found experimentally. The explanation of many of these differences cannot be given, but a suggestion made by Nernst[1] will doubtless account for some of them. As he says, in the development of Van der Waals' equation, the assumption is always made that in the passage from the gaseous to the liquid condition, and *vice versa*, there is no change in the molecular condition. We know, however, at present that this assumption is not true. Many substances in passing from gas to liquid form complex molecules to a greater or less extent. As we shall see later, it has been shown that the molecules of liquid water are made up of four of the simplest molecules, while the molecule of water-vapor is the simplest possible. We shall also see that the molecules of many substances in the liquid state are complex, while in the gaseous state the molecule is generally the simplest conceivable. On account of the very incomplete state of our knowledge with respect to the molecular weights of substances in the liquid condition, it is impossible to say at present whether molecular aggregation in the liquid state can account for all of the deviations of liquids from the equation of Van der Waals.

In this section the attempt has been made to point out the most striking relations between liquids and gases, and in doing this some general properties of liquids have been considered. We must now study the several properties of liquids more closely, and especially any relations which may exist between properties and chemical composition on the one hand, and properties and constitution on the other. Indeed, it was right in this field that much of the earlier physical chemical work was done. The question was raised, and answered as far as possible, how does the introduction of a CH_2 group, or of an oxygen or chlorine atom, affect the physical properties of the compound into which it enters? Or what is the difference between the effect on one compound produced by a given atom or group, and the effect on other compounds? Then the question of the effect on physical properties of an atom or group in one state of combination, as compared with the effect produced by the same atom or group in a different state of combination, arose. What, for example, would be the effect on the physical properties of compounds produced by an oxygen atom in the hydroxyl condition, with respect to an oxygen atom in the carbonyl condition? In a word, how would constitution affect properties?

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[1] See Nernst: *Theoretische Chemie*, p. 237.

A great many interesting and important relations between composition and properties, and constitution and properties have been discovered. Most of this work has been done, as we would expect, with liquids, and will, therefore, be taken up in this chapter. We shall now take up in turn the thermal properties of liquids, the optical properties, and, in addition, a number of more or less apparently disconnected physical properties of liquids; and shall especially point out in every case the more important relations which have been discovered between the property in question and chemical composition and constitution.

THE VAPOR-PRESSURE AND BOILING-POINT OF LIQUIDS

The Vapor-pressure of Liquids. — When a liquid is in contact with free space, it continually sends off particles into this space, as we have seen. Given a liquid in contact with an inclosed space; particles are constantly escaping from the surface of the liquid, but at the same time vapor-particles are condensing. Finally, an equilibrium will be established between the liquid and its vapor, when the same number of particles escape in unit time as condense in the same time. The vapor-pressure exerted by a liquid is the pressure of its vapor when this condition of equilibrium has been reached.

The condition of equilibrium varies, as we have seen, with the temperature, and the vapor-pressure also varies; the higher the temperature the greater the vapor-pressure. In speaking of the vapor-pressure of liquids we must, then, always state the temperature to which the vapor-pressure refers. In comparing the vapor-pressures of liquids we could select some temperature and measure the pressures of their vapors at this temperature; this method has been extensively used.

The liquid whose vapor-pressure it is desired to measure is placed most conveniently above the mercury in the vacuum of a barometer tube, and brought to the desired temperature. The column of mercury is depressed, and the amount of the depression is measured by reading the height of the mercury in the tube and also on a second barometer. From the difference in the height of the two columns the vapor-pressure of the liquid at the temperature in question is determined by reduction to normal conditions.

The objection to this method, which has been termed the statical method, is that the presence of any volatile impurity in the liquid would greatly vitiate the results. The vapor-pressure of the impurity would add itself to that of the pure liquid, giving a vapor-pressure which is too great. This error may be very considerable if there is only a trace of the impurity present, as Tammann[1] has shown.

A far better method, and one which can be used at much higher temperatures and pressures, is that known as the dynamical method. The principle is very different from that of the statical method. In the latter, as we have just seen, the temperature is kept constant and the vapor-pressures of the different liquids measured at this constant temperature. In the dynamical method the pressure is maintained constant over the different liquids, and the temperatures at which they boil determined accurately by means of fine thermometers. In the statical method we measure vapor-pressures, while in the dynamical method we measure temperatures. Any convenient pressure can be chosen, and the temperature at which liquids boil under this pressure can be measured. The pressure must be very carefully regulated, since the boiling-point of a liquid is greatly affected by comparatively slight changes in pressure.

The results obtained by the two methods for perfectly pure substances agree very closely, showing that there is for any liquid a definite vapor-pressure for any given temperature. The apparent differences between the results of the two methods have been shown to be due to the large error produced by traces of volatile impurities, when the statical method is used.[2]

A number of attempts have been made to formulate the relation between vapor-pressure and temperature,[3] but none of these has been entirely successful. The expressions which hold at one temperature generally do not hold at other temperatures.

Relations between the Vapor-pressures of Different Substances. — More interesting are the relations which have been discovered between the vapor-pressures of different substances. Dalton[4] thought that the vapor-pressures of all liquids, at temperatures equally distant from their boiling-points, were equal. While this holds approximately for certain classes of substances, it is far from the truth in many cases. The expression proposed by Dühring is more rational, and holds in a much larger number of cases. The vapor-pressures are equal at temperatures which are at proportional distances from the boiling-points.

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[1] *Wied. Ann.* **32**, 683 (1887).

[2] Ramsay and Young: *Ber. d. chem. Gesell.* **18**, 2855 (1885); **19**, 69, 2107 (1886); **20**, 67 (1887).

[3] *Compt. rend.* **104**, 1568 (1887).

[4] *Mem. Lit. Phil. Soc.* Manchester, **5**, 550.

The formula expressing the generalization of Dühring is:—

$$t' = t'' - 100f + ft = t'' + f(t - 100).$$

t' is the boiling-point of the substance under the pressure in question; t'' its boiling-point under a pressure of 76 cm. of mercury, and t and 100 the corresponding temperatures for water; f is a constant factor.

Dühring showed that this equation holds approximately in many cases; but that there are striking exceptions was pointed out by Winkelmann.[1] The latter,[2] in turn, proposed an expression for the relation between vapor-pressure and temperature, which is independent of the nature of the substance; but reference only can be made to it.

The relation discovered by Ramsay and Young[3] should, however, receive closer attention. If R is the ratio of the absolute temperatures of the two bodies, corresponding to any vapor-pressure which is the same for both of them; R' the ratio at any other pressure, which again is the same for both; t and t' the temperatures of one of the bodies corresponding to the two vapor-pressures, and c a constant with a small plus or negative value, or may equal zero; then

$$R' = R + c(t' - t).$$

When $c = 0$, $R' = R$, which means that the ratio between the absolute temperatures is a constant at all vapor-pressures. If c has a small positive or negative value this can readily be calculated. Ramsay and Young showed, by comparing a dozen or fifteen substances with one another, that their formula agrees with the facts to within a comparatively small limit. They[4] tested still further the relation between the absolute temperatures of equal vapor-pressures, expressed by their equation. Using the determinations of the vapor-pressures of many esters, made by Schumann,[5] and calculating the ratios of the absolute temperatures of all of them to those of ethyl acetate at the same pressure, it was found for pressures ranging from 200 to 1300 mm., that the ratio of the absolute temperatures is a constant at all pressures. This is shown by a few results taken from the paper of Ramsay and Young.

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[1] *Wied. Ann.* **9**, 391 (1880).

[2] *Ibid.* **9**, 208 (1880).

[3] *Phil. Mag.* **21**, 33 (1886).

[4] *Ibid.* **22**, 32 (1886).

[5] *Wied. Ann.* **12**, 40 (1881).

Pressures

	200 MM.	760 MM.	1300 MM.	MEAN.
Methyl formate	.8706	.8720	.8715	.8714
Ethyl formate	.9323	.9352	.9344	.9340
Methyl acetate	.9431	.9440	.9420	.9430
Propyl acetate	1.0690	1.0677	1.0678	1.0682
Methyl propionate	1.0073	1.0080	1.0073	1.0075
Ethyl propionate	1.0614	1.0605	1.0615	1.0611
Methyl butyrate	1.0716	1.0720	1.0724	1.0720
Ethyl isobutyrate	1.0935	1.0943	1.0953	1.0944
Methyl valerate	1.1139	1.1131	1.1135	1.1135
Ethyl valerate	1.1619	1.1634	1.1642	1.1632

From the mean ratio for each ester between its absolute temperature and that of ethyl acetate at the same pressure, and from the temperatures of ethyl acetate at the three pressures, the boiling-points of the twenty-seven esters were calculated. The results are given by them in a table, together with the temperatures as determined experimentally. In no case does the calculated value differ from the observed by more than 0°.7. This is, of course, a striking confirmation of the general truth of the relation pointed out in the equation of Ramsay and Young.

Relations between Boiling-points and Composition and Constitution. The Work of Kopp. — The relations between composition and constitution and boiling-points have been extensively investigated among the organic liquids. Kopp,[1] as early as 1842, extended his investigations of other physical properties of substances to their boiling-points, and discovered comparatively simple relations between the boiling-points of liquids and their composition. He showed that as the compound increases in complexity the boiling-point is raised. An ethyl compound boils about 19° C. higher than the corresponding methyl compound. A little later in the same year[2] he formulated his generalization, that *equal differences in the composition of organic compounds correspond to equal differences in the boiling-point.* This would be very remarkable if it were true, but we shall see that it is only an approximation.

If the law of Kopp was rigidly true, then, isomeric compounds, since they have the same composition, must boil at the same temperature. Kopp pointed out in 1844[1] that this is not the case. Ethyl acetate and butyric acid are isomeric, yet the former boils 82° lower than the latter. These isomeres, however, are not of similar constitution. He determined, then, the boiling-points of isomeric substances whose constitutions are similar.

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[1] *Lieb. Ann.* **41**, 79 (1842).

[2] *Ibid.* **41**, 169 (1842).

		BOILING-POINT
Methyl acetate,	CH_3COOCH_3	56°
Ethyl formate,	$HCOOC_2H_5$	55°
Methyl valerate,	$CH_3CH_2CH_2CH_2COOCH_3$	115°
Amyl formate,	$HCOOC_5H_{11}$	116°
Ethyl butyrate,	$CH_3CH_2CH_2COOC_2H_5$	115°

It would appear from these results that isomeric substances having similar constitution have the same boiling-point, to within the limit of experimental error.

In 1855 Kopp[2] published the results of an elaborate investigation on the boiling-points of organic liquids. He included in this work a number of alcohols, acids, and ethereal salts. A few of his results will show that his conclusions are substantiated by the facts.

		BOILING-POINT	
Methyl alcohol,	CH_4O	65°	
			13°
Ethyl alcohol,	C_2H_6O	78°	
			18°
Propyl alcohol,	C_3H_8O	96°	
			13°
Butyl alcohol,	$C_4H_{10}O$	109°	
Formic acid,	$HCOOH$	105°	
			12°
Acetic acid,	CH_3COOH	117°	
			25°
Propionic acid,	C_2H_5COOH	142°	
			14°
Butyric acid,	C_3H_7COOH	156°	
Ethyl formate,	$HCOOC_2H_5$	55°	
			19°
Ethyl acetate,	$CH_3COOC_2H_5$	74°	
			22°
Ethyl propionate,	$C_2H_5COOC_2H_5$	96°	

Kopp[3] drew the general conclusion from this work that, "for homologous compounds belonging to the same series, the difference in boiling-points is, in general, proportional to the difference in composition. The difference in boiling-point, corresponding to the difference in composition of CH_2, is the same in many series of compounds, and is equal to 19."

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[1] *Lieb. Ann.* **50**, 71 (1844).

[2] *Ibid.* **96**, 1 (1855).

[3] *Ibid.* **96**, 32 (1855).

Work since the Time of Kopp. — More accurate experimental work has subsequently shown that there is no law connecting the boiling-points of substances and their composition and constitution. Indeed, it would be most remarkable if any such law did exist, since the boiling-points of liquids are the temperatures, measured from the freezing-point of water, at which their vapor-pressures just overcome the atmospheric pressure. These boiling-points evidently bear no close relation to any fundamental property of the compound, and, therefore, are not, strictly speaking, comparable temperatures.

While no generalization worthy of the name of law connects the boiling-points of substances with their composition and constitution, a number of relations between them have been found to exist. Dittmar[1] showed that the two isomeric substances, ethyl formate and methyl acetate, do not have the same vapor-tension at the same temperature, that of ethyl formate being the greater throughout. He gives the temperatures of equal vapor-pressures, and they are as follows: —

Ethyl formate . . .	20°	26°	33°	43°	53°
Methyl acetate . . .	21°.7	27°.8	34°.7	44°.5	54°.4

The boiling-point of methyl acetate is, therefore, higher than that of ethyl formate.

That isomeric compounds do not boil at the same temperature, but, if they have similar constitution, boil at nearly the same temperature, is shown by the following examples: —

	Boiling-point
Octyl formate, $C_9H_{18}O_2$	198°.1
Heptyl acetate, $C_9H_{18}O_2$	191°.3
Amyl butyrate, $C_9H_{18}O_2$	184°.8
Butyl valerate, $C_9H_{18}O_2$	185°.8

Kopp supposed, as we have seen, that within a homologous series of compounds a constant difference in composition corresponds to a constant difference in boiling-point. This was found by Schorlemmer[2] not to be true for the normal paraffine hydrocarbons and some of their derivatives, as the following results will show. *b.-p.* represents the boiling-point, and *d.* the difference between the boiling-points of two successive members of a homologous series.

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[1] *Lieb. Ann. Suppl.* **6**, 328 (1868).

[2] *Lieb. Ann.* **161**, 263 (1872).

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	b.-p.	*d.*
C_4H_{10}	1°	37°
C_5H_{12}	38°	32°
C_6H_{14}	70°	29°
C_7H_{16}	99°	25°
C_8H_{18}	124°	

	b.-p.	*d.*
C_2H_5Cl	12°.5	33°.9
C_3H_7Cl	46°.4	31°.2
C_4H_9Cl	77°.6	28°.0
$C_5H_{11}Cl$	105°.6	

	b.-p.	*d.*
C_2H_5Br	39°.0	32°.0
C_3H_7Br	71°.0	29°.4
C_4H_9Br	100°.4	28°.3
$C_5H_{11}Br$	128°.7	

	b.-p.	*d.*
CH_3I	40°.0	32°.0
C_2H_5I	72°.0	30°.0
C_3H_7I	102°.0	27°.6
C_4H_9I	129°.6	25°.8
$C_5H_{11}I$	155°.4	

	b.-p.	*d.*
C_2H_6O	78°.4	18°.6
C_3H_8O	97°.0	19°.0
$C_4H_{10}O$	116°.0	21°.0
$C_5H_{12}O$	137°.0	19°.0
$C_6H_{14}O$	156°.6	

It follows from these results that as the compounds become more complex, the difference between the boiling-points of two succeeding members of a homologous series becomes less. This is what we would naturally expect, since the larger the number of carbon and hydrogen atoms in the molecule the smaller the influence of a CH_2 group when introduced into the compound. This same relation is brought out by Zwicke and Franchimont,[1] though perhaps in not quite so striking a manner, in connection with the acids of the paraffine series and some of their esters.

		BOILING-POINT		BOILING-POINT OF ETHYL ETHER	
Acetic acid,	CH_3COOH	118°.0	22°.6	77°.0	21°.8
Propionic acid,	C_2H_5COOH	140°.6	21°.7	98°.8	22°.2
Butyric acid,	C_3H_7COOH	162°.3	21°.7	121°.0	2 × 23°.0
Valeric acid,	C_4H_9COOH	184°.0	21°.0		
Caproic acid,	$C_5H_{11}COOH$	205°.0	16°.0	167°.0	20°.0
Œnanthylic acid,	$C_6H_{13}COOH$	221°.0		187°.0	

The decrease in the difference between the boiling-points of successive members of homologous series of compounds with increase in complexity, was found also by Linnemann.[2] As the result of his more accurate investigations he concluded that "the difference between the boiling-points decreases, in most of the series thus far studied, with increasing number of carbon atoms, at least among the earlier members of the series."

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[1] *Lieb. Ann.* **164**, 333 (1872).

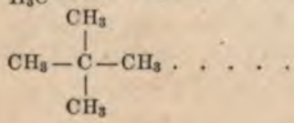
[2] *Ibid.* **162**, 39 (1872).

The effect of constitution on boiling-point is clearly shown by the substituted hydrocarbons of the benzene series. If one hydrogen of the benzene ring is substituted by a group, the resulting compound has a different boiling-point from its isomeric compound with two hydrogen atoms in the benzene ring substituted by two groups. When three hydrogen atoms in the benzene ring are substituted by three groups, the compound has a still different boiling-point. This is seen from the following data taken from the work of Kopp: —

	b.-p.		b.-p.		b.-p.
$C_6H_5 \cdot C_2H_5$	133°–135°	$C_6H_4 < \begin{matrix} CH_3 \\ CH_3 \end{matrix}$	139°–140°		
$C_6H_5 \cdot C_3H_7$	151°–153°	$C_6H_4 < \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}$	159°–160°	$C_6H_3 \begin{matrix} / CH_3 \\ - CH_3 \\ \backslash CH_3 \end{matrix}$	165°–166°
$C_6H_5 \cdot C_4H_9$	—	$C_6H_4 < \begin{matrix} CH_3 \\ C_3H_7 \end{matrix}$	175°–178°	$C_6H_3 \begin{matrix} / CH_3 \\ - CH_3 \\ \backslash C_2H_5 \end{matrix}$	183°–184°
		$C_6H_4 < \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}$	178°–179°		

By comparing the boiling-points of isomeric substances enclosed between the same horizontal lines, it at once becomes apparent that constitution has a marked influence on boiling-point in this series of hydrocarbons. The larger the number of hydrogen atoms substituted by groups, the higher the boiling-point of the resulting compound.

That constitution has a marked influence on boiling-point has also been pointed out by Naumann.[1] His paper deals with the hydrocarbons of the paraffine series and some of their derivatives, including some alcohols, aldehydes, ketones, and acids. A few metameric compounds are taken from the table given by Naumann.

		b.-p.
Normal pentane,	$CH_3 . CH_2 . CH_2 . CH_2 . CH_3$.	38°
Isopentane,	$\begin{matrix} H_3C \\ H_3C \end{matrix} > CH . CH_2CH_3$ . . .	30°
Tetramethyl methane,	 $CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}} - CH_3$	9°.5

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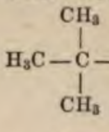
[1] *Ber. d. chem. Gesell.* 7, 173 (1874).

		b.-p.
Normal butyl alcohol,	$CH_3 . CH_2 . CH_2 . CH_2OH$ . .	116°
Isobutyl alcohol,	$\genfrac{}{}{0pt}{}{H_3C}{H_3C}\!>CH . CH_2OH$ . . .	109°
Secondary butyl alcohol,	$CH_3 . CH_2 . CHOH . CH_3$ . .	99°
Tertiary butyl alcohol,	 $H_3C-\overset{\overset{\Large CH_3}{\vert}}{\underset{\underset{\Large CH_3}{\vert}}{C}}-OH$	82°.5

The normal compounds, or those with a chainlike structure, have the highest boiling-points. The larger the number of side chains, the lower the boiling-point of the compound. This is sometimes expressed by saying, the more symmetrical the compound the lower its boiling-point. Naumann[1] attempts to explain the higher boiling-point of the normal compounds as due to their chainlike structure. The molecules constructed in this way make better contact than when there are side chains to the molecules, and the larger the number of side chains the poorer the contact between the molecules. The better the contact between the molecules, the higher will be the temperature required to tear the molecules apart and send them off as vapor; consequently, the more nearly the compound conforms to the chain structure, the higher will be its boiling-point.

In the light of our present conceptions of structure and of the energy relations in substances, this explanation cannot be very seriously considered.

We have, on the other hand, already seen that the greater the number of substituting groups in the benzene hydrocarbons, the higher the boiling-point. This apparent discrepancy between the two series of compounds need occasion no great surprise, if we consider the very different constitutions of the paraffines and benzene compounds.

Of the isomeric substitution products of benzene the ortho compounds in general boil higher than the meta, and these, in turn, a little higher than the para compounds. This again is only an approximate relation, to which many exceptions are known.

Effect of Certain Atoms or Groups on the Boiling-point of Liquids. — The boiling-points of compounds are affected with some regularity by the introduction of certain atoms or groups. Thus, the introduction of a chlorine atom into a methyl group raises the boiling-point of the compound about 60° to 65°. The introduction of a second or third chlorine atom has a much less marked influence on the boiling-point. This is shown by acetic acid and its chlorine substitution products.

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[1] *Ber. d. chem. Gesell.* 7, 173 (1874).

	b.-p.	*d.*
Acetic acid, CH_3COOH	118°.0	67°.0
Monochloracetic acid, $CH_2ClCOOH$	185°.0	9°.0
Dichloracetic acid, $CHCl_2COOH$	194°.0	4°.0
Trichloracetic acid, CCl_3COOH	198°.0	

A rise in boiling-point is produced when chlorine is replaced by bromine, and a still further rise when bromine is replaced by iodine.

It should be observed that most of the relations pointed out between boiling-points and composition and constitution are only regularities, which hold in a large majority of cases. Exceptions to many of these are not wanting. Thus, hydrogen replaced by chlorine generally means that the chlorine substitution product will boil higher than the original substance, but Henry[1] has shown that when the hydrogen in acetonitrile is replaced by chlorine the monochlornitrile boils higher than the original compound. When the second and third hydrogen atoms of the nitrile are replaced by chlorine, the resulting compounds boil lower than the monochlor derivative, and the trichlornitrile boils almost as low as the original nitrile itself.

	b.-p.		*b.-p.*
CH_3CN	81°	$CHCl_2CN$	112°
CH_2ClCN	123°	CCl_3CN	83°

In dealing with these regularities in boiling-points we must remember that they are only the first approximations to the truth. We should scarcely speak of them as generalizations, unless in a very narrow and imperfect sense, and still less should we regard them as laws of nature. We should consider them as the pioneer efforts in a direction which some day will lead to a fundamental and deep-seated generalization, which will throw much light on the inter- and intra-molecular condition of matter.

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[1] *Ber. d. chem. Gesell.* **6**, 734 (1873).

HEAT OF VAPORIZATION

Heat of Vaporization. Methods of Determining. — We have seen in the preceding section that quite different temperatures are required to convert different liquids into vapor at the same pressure; the boiling-points of liquids are very different. We shall now learn that very different amounts of heat are required to convert comparable quantities of liquid into vapor.

Whenever a liquid is converted into vapor, a large amount of heat disappears as such. A part of this is consumed in doing work in driving back the air, since a small volume of liquid occupies a comparatively large volume in the form of vapor. The amount of this work can be easily calculated, knowing the pressure of the air and the volume of the vapor formed. It has been found that only a small part of the heat that disappears in vaporization is consumed in doing external work; the larger part does internal work in the liquid, transforming it from the liquid to the gaseous condition.

In measuring the heat of vaporization of a liquid, we can either measure the amount of heat required to convert a given quantity of the liquid into vapor at the same temperature as that of the liquid, or we can condense the vapor to liquid and measure the amount of heat liberated during the process of condensation, since we know that the heat liberated in condensation is exactly equal to that consumed in vaporization. It is far simpler to measure the heat liberated during condensation, and this has been done. The apparatus devised by Schiff[1] has some advantages over that constructed several years earlier by Berthelot.[2] If the vapor is condensed in a calorimeter containing water at ordinary temperatures, the heat given up to the calorimeter is that required to vaporize the liquid, plus the heat consumed in raising the liquid from the temperature of the calorimeter to its own boiling-point. The latter quantity must be subtracted from the total heat as measured in the calorimeter to obtain the heat of vaporization of the liquid.

Relations between Heats of Vaporization. The Law of Trouton. — To discover any relations which may exist between the heats of vaporization of different substances, we must deal with comparable quantities of substances. It is most convenient to use gram-molecular quantities, and we would then have to do with molecular heats of vaporization. An extremely interesting and probably very important relation between the molecular heats of vaporization of different substances was discovered by Trouton.[1] *The molecular heats of vaporization are proportional to the absolute temperatures at which the liquids boil.*

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[1] *Lieb. Ann.* **234**, 338 (1886). [2] *Ann. Chim. Phys.* [5], **12**, 550 (1877).

That this relation is very nearly true is seen from the following data, taken from the work of Schiff.[2] Mh is the molecular heat of vaporization, and T the absolute boiling temperature of the substance.

	BOILING-POINT	HEAT OF VAPORIZATION	$\frac{Mh}{T}$
Ethyl formate, $C_3H_6O_2$	53°.5	92.2 cal.	20.8
Ethyl acetate, $C_4H_8O_2$	77°.0	83.1 "	20.8
Ethyl propionate, $C_5H_{10}O_2$	98°.7	77.1 "	21.0
Methyl butyrate, $C_5H_{10}O_2$	102°.3	77.3 "	20.9
Methyl valerate, $C_6H_{12}O_2$	116°.3	70.0 "	20.9
Ethyl valerate, $C_7H_{14}O_2$	134°.0	64.7 "	20.6
Isoamyl acetate, $C_7H_{14}O_2$	142°.0	66.4 "	20.7
Isoamyl isobutyrate, $C_9H_{18}O_2$	169°.0	57.9 "	20.6
Benzene, C_6H_6	80°.35	93.5 "	20.6
Toluene, C_7H_8	116°.8	83.6 "	20.0
Meta-xylene, C_8H_{10}	139°.9	78.3 "	20.0
Mesytilene, C_9H_{12}	162°.7	71.8 "	19.8
Cymene, $C_{10}H_{14}$	175°.0	66.3 "	19.8

It will be seen at once that the value of $\frac{Mh}{T}$ is obtained for any compound, by multiplying its heat of vaporization by its molecular weight to obtain the molecular heat of vaporization, and dividing this by the boiling-point of the substance plus 273°.

These results, which are a few taken from many, show to within what limits the law of Trouton holds good for these classes of substances. Ostwald[3] has calculated, from the measurements of others, the ratio $\frac{Mh}{T}$ for entirely different classes of substances: —

	BOILING-POINT	HEAT OF VAPORIZATION	$\frac{Mh}{T}$
Nitric acid, HNO_3	86°	72.5	20.2
Bromine, Br_2	63°	75.7	22.5
Ethylene bromide, $C_2H_4Br_2$	111°	82.3	21.5
Ethyl bromide, C_2H_5Br	41°	67.2	21.4
Methylene chloride, CH_2Cl_2	40°	64.0	20.5
Sulphur dioxide, SO_2	− 18°	59.0	23.1
Cyanogen, C_2N_2	−21°	56.3	22.4

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[1] *Phil. Mag.* **18**, 54 (1884).

[2] *Lieb. Ann.* **234**, 338 (1886).

[3] *Lehrb. d. allg. Chem.* **1**, 355.

The molecular heats of vaporization are expressed in units which are one hundred times as large as those in the above table.

The law of Trouton is thus shown to hold very closely for a number of classes of substances. While we at present do not see the full significance of this relation between heat of vaporization and absolute boiling-point of a substance, we cannot escape the conviction that it is the expression of some principle of profound significance, connecting the energy relations of the liquid and gaseous states of aggregation.

Heat of Vaporization at the Critical Point. — We have seen that the critical point is that at which all differences between the liquid and its saturated vapor disappear. It is, therefore, necessary that at the critical point the heat of vaporization should become zero. This has been verified experimentally by Mathias.[1] He devised a constant temperature method, applied it to sulphurous acid, carbon dioxide, and nitrous oxide, and showed at least in the case of carbon dioxide, that *at the critical point the latent heat* (heat of vaporization) *is absolutely zero.* This is another interesting condition which obtains at that very remarkable point, known as the critical point of a liquid.

SPECIFIC HEAT OF LIQUIDS

Specific Heat of Liquids. Methods of Determining. — Just as the amount of heat required to convert comparable quantities of different liquids into vapor varies for every liquid, so, also, the amount of heat consumed in raising a liquid through any given range of temperature varies from one liquid to another. The relative amounts of heat required to raise unit quantities of different substances through the same range of temperature are known as the specific heats of the substances in question. Water is taken as the unit, and the specific heats of other substances compared with the specific heat of water. The amount of heat required to raise the temperature of one gram of water from 0° to 1° C. is termed a calorie.[2] The quantity of heat required to raise the temperature of one gram of any substance the same amount, expressed in calories, is the specific heat of the substance referred to water as unity.

The earlier methods of determining specific heats consisted in bringing the substance whose specific heat was to be determined, at a known temperature, in contact with a substance whose specific heat was known; the temperature of the latter being different from that of the former. The resulting temperature was determined, and from these data the specific heat of the substance in question could be calculated. Since water is taken as the unit in measuring specific heats, the substance in question was usually mixed with water and the resulting temperature determined. From the nature of this method it has been termed the "method of mixtures." It is obvious that a number of corrections must be introduced, as in all calorimetric measurements, for the specific heat of the vessel, etc.

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[1] *Ann. Chim. Phys.* [6], **21**, 69 (1890).

[2] Other definitions of the calorie are given. These will be considered under thermochemistry.

Bunsen[1] devised an ice-calorimeter which has been used for measuring specific heats. From the amount of ice melted by a given quantity of any substance at a definite temperature, it is easy to calculate the specific heat of the substance. It is of course necessary in using this method to know the heat of fusion of ice, but this has been fairly accurately determined as 79.7 calories.

The Specific Heat of Water. — Since the specific heat of water is taken as the unit, it is especially important that this quantity should be most accurately determined at different temperatures. It was found by Regnault, and by a number of investigators since his time, that the specific heat of water is not a constant for different temperatures. Very different results have been obtained from time to time by different experimenters. Some found that the specific heat of water increased with the temperature, others that there were irregularities at about 4° C., and others still that the specific heat decreased up to a certain temperature and then began to increase. Among the most accurate determinations of the specific heat of water which have ever been made, if not the most accurate, are those of Rowland.[2] In connection with his determination of the mechanical equivalent of heat he reinvestigated the problem and found that the specific heat of water decreases from 5° C. up to about 30° C., and then began to increase again. The results of Rowland are given in the following table, together with those more recently obtained by Lüdin:[3] —

	ROWLAND'S RESULTS	LÜDIN'S RESULTS
0°	——	1.0051
5°	1.0054	1.0027
10°	1.0019	1.0010
15°	1.0000	1.0000
20°	0.9979	0.9994
25°	0.9972	0.9993
30°	0.9969	0.9996
35°	0.9981	1.0003

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[1] *Pogg. Ann.* **141**, 1 (1870).

[2] *The Mechanical Equivalent of Heat*, p. 120.

[3] *Dissertation*, Zürich, 1895.

Rowland[1] says in connection with his results, which show that the specific heat of water decreases at first and then begins to increase: "However remarkable this fact may be, being the first instance of the decrease of the specific heat with rise of temperature, it is no more remarkable than the contraction of water to 4°."

Relations between Composition and Constitution, and Specific Heats. — To determine whether any simple relations exist between the composition and constitution of substances and their specific heats, we must again deal with comparable quantities of substances. We employ gram-molecular quantities of substances; and when we multiply the specific heat of the substance referred to one gram by the molecular weight of the substance, we obtain its *molecular heat.* The molecular heats of a number of homologous series of compounds have been calculated by Ostwald[2] from their specific heats as determined by Reis.[3] The molecular heats of a few substances will be given to show the relations which have been observed.

		MOLEC. HEAT	
Methyl alcohol,	CH_4O	21.0	
			9.3
Ethyl alcohol,	C_2H_6O	30.3	
			10.2
Propyl alcohol,	C_3H_8O	40.5	
			10.4
Butyl alcohol,	$C_4H_{10}O$	50.9	
			9.6
Amyl alcohol,	$C_5H_{12}O$	60.5	
Propyl chloride,	C_3H_7Cl	31.6	
Propyl bromide,	C_3H_7Br	32.3	
Propyl iodide,	C_3H_7I	34.3	

		MOLEC. HEAT	
Formic acid,	$HCOOH$	24.2	
			7.4
Acetic acid,	CH_3COOH	31.6	
			2 × 7.9
Butyric acid,	C_3H_7COOH	47.4	
Benzene,	C_6H_6	33.8	
			8
Toluene,	C_7H_8	41.8	
			7
Ethylbenzene,	C_8H_{10}	48.8	
			8
Mesitylene,	C_9H_{12}	56.8	

These results show that for homologous series of compounds a constant difference in composition (CH_2), corresponds approximately to a constant difference in molecular heat. The molecular heats of the three halogens do not differ very considerably, yet there is a slight increase from the chloride to the bromide to the iodide.

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[1] *The Mechanical Equivalent of Heat*, p. 131.

[2] *Lehrb. d. Allg. Chem.* II, p. 585.

[3] *Wied. Ann.* **13**, 447 (1881).

The effect of constitution on molecular heats is shown by the following isomeric substances: —

	Molec. Heat
Butyric acid, $C_4H_8O_2$	47.4
Isobutyric acid, $C_4H_8O_2$	47.6
Allyl alcohol, C_3H_6O	38.1
Propyl aldelyde, C_3H_6O	32.6

If the constitution of isomeric substances does not differ greatly, the molecular heats are not very different. If, however, the isomeres have constitutions which are very different, the molecular heats may differ widely from one another.

The relation between composition and specific heat, which was brought out by the work of Reis, was shown by Schiff[1] not to apply to all classes of compounds. Indeed, a marked exception was observed in the case of the esters of the fatty acids. *"All the esters of the fatty acids have, at the same temperatures, and, therefore, also at the same absolute temperatures, equal specific heats."* He investigated some twenty-seven of these esters, and also a number of other classes of compounds, including aromatic hydrocarbons, fatty acids, and a number of alcohols.

As the result of this work Schiff announced what he termed a law[2] for all the esters having the formula $C_2H_{2n}O_2$.

"Equal weights at equal absolute temperatures have equal heat capacities."

"Equal volumes at equal fractions of the absolute critical temperature have equal heat capacity."

The relations between specific heats and composition and constitution, like the relations between boiling-points and composition and constitution, must be regarded as only approximations. When these quantities have been more extensively and accurately measured, we may be able to arrive at some wide-reaching generalization, connecting specific heats with the chemical nature of the substances in question.

We have thus far studied some thermal properties of liquids — boiling-points, heat of vaporization, and specific heats. Certain optical properties of pure liquids will now be taken up.

[1] *Lieb. Ann.* **234**, 300 (1886). *Ztschr. phys. Chem.* **1**, 376 (1887).

[2] *Lieb. Ann.* **234**, 331 (1886).

THE REFRACTIVE POWER OF LIQUIDS

Refraction of Light. Index of Refraction. — When a ray of light passes from one medium into another of different density, it is bent out of its course, or, as we say, refracted. For light passing from any given medium into another, there is a constant relation between the sine of the angle of incidence and the sine of the angle of refraction. This ratio is termed the index of refraction of the substance. If we represent the angle of incidence by i, and the angle of refraction by r, the index of refraction, n, is expressed thus: —

$$n = \frac{\sin i}{\sin r}.$$

This expresses the index of refraction of the one medium with respect to the other, and is also the ratio between the velocities of monochromatic light in the two media.

If we choose some medium as the standard and determine the indices of refraction of other media in terms of this standard, the results will be comparable with one another. In practice the air is chosen as the most convenient standard, since light is passed through the air and then through the medium whose refractive power is to be determined.

Several methods have been devised for determining the refractive power of liquids. In one[1] a hollow prism is filled with the liquid, and the amount by which the ray of light is bent out of its course in passing through the liquid is determined by means of the spectrometer.

A more convenient method, especially for use with liquids, is based upon a somewhat different principle. When a ray of light passes from a more refracting to a less refracting medium, there is a limit to the angle of incidence at which refraction will take place. Beyond this angle the ray will not enter the less refracting medium at all, but will be totally reflected. The value of this angle depends upon the relative refractive powers of the two media. This principle has been made use of by Pulfrich[2] for determining the relative refractive powers of substances. The Pulfrich refractometer consists essentially of a rectangular prism of strongly refracting glass, on whose horizontal surface there is a small glass cylinder to receive the liquid to be studied. The monochromatic light enters the liquid nearly parallel to the horizontal surface of the prism. Only those rays can enter the prism from the liquid whose angle of emergence is less than the angle of total reflection. The apparatus is provided with a telescope and graduated circle. The telescope moves in a vertical plane, until it is just on the border between light and dark, and in this way the angle of emergence is determined. The size of this angle depends upon the relative indices of refraction of the liquid and the prism. If we represent this angle by e, the index of refraction of the liquid by n, and that of the prism by N, we have,—

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[1] *Pogg. Ann.* **98**, 91 (1856).

[2] *Ztschr. f. Instrumentenkunde*, **8**, 47; **15**, 389. *Ztschr. phys. Chem.* **18**, 294 (1895).

$$n = \sqrt{N^2 - \sin^2 e}.$$

This apparatus has a number of advantages over all other forms for determining indices of refraction. It is very simple to use, and gives accurate results; it requires but little time to measure the refractive power of any liquid; and a small quantity of the substance suffices, since it is only necessary to cover that portion of the surface of the prism enclosed within the cup. Reference[1] only can be made to other applications of the Pulfrich refractometer. The refractive power of liquids is affected by temperature and wave-length of light, so that these must be kept constant to obtain comparable results.

Refractivity and Density. — A number of formulas have been proposed connecting the index of refraction of a substance with its density. Biot and Arago in 1806 proposed for gases the formula $\frac{n^2-1}{d} = \text{const.}$, based on the emission hypothesis of light. The theoretical foundations for this formula failed to exist after the emission hypothesis was overthrown, and it was also shown by direct experiment to be a very rough approximation, holding only in a limited number of cases.

Gladstone and Dale[2] found an empirical expression which was very much more nearly in accord with experimental results. Their equation is,—

$$\frac{n-1}{d} = \text{const.}$$

Landolt[3] tested this formula at different temperatures and found that it held very closely for many substances. He also applied this equation to mixtures, and found that it held more satisfactorily than any other formula proposed up to that time.

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[1] Le Blanc: *Ztschr. phys. Chem.* **10**, 433 (1892).

[2] *Phil. Trans.* (Lond.), 1858.

[3] *Lieb. Ann. Suppl.* **4**, 1 (1865).

After the undulatory theory of light was established, there was no formula based on any theoretical foundation connecting the index of refraction with the density of the substance. This was furnished independently by H. A. Lorentz[1] and L. Lorenz.[2] Lorentz, from a mathematical consideration of the electromagnetic theory of light, deduced the equation —

$$\frac{n^2-1}{n^2+2}\,\frac{1}{d}=\text{const.},$$

while Lorenz in Copenhagen derived the same formula from the undulatory theory of light.

Since the formula of Lorentz-Lorenz was proposed, much work has been done comparing the results of this formula with those of the formula of Gladstone and Dale. On the whole the latter expression seems to fit the facts quite as well as the more complex formula. Dufet, in 1885, and Sutherland,[3] in 1889, furnished a theoretical demonstration of Gladstone's law.

Quite recently another expression has been proposed connecting density and refractivity. Edwards[4] suggested the formula —

$$\frac{n-1}{nd}=\text{const.},$$

and showed that it held approximately for a number of compounds, over a considerable range both of temperature and concentration.

None of the formulas proposed agree entirely satisfactorily with the facts. Indeed, it is not at all certain that there exists any exact relation between refractivity and density, which can be expressed by a simple formula. Of the formulas proposed, the simplest and probably on the whole the best is that of Gladstone and Dale, and Landolt, —

$$\frac{n-1}{d}=\text{const.}$$

This expression $\frac{n-1}{d}$ is termed the *specific refractivity*. When this is multiplied by the molecular weight of the substance M, we have the *molecular refractivity* $= M\frac{n-1}{d}$. For the purpose of discovering relations between the refractivities of substances we must compare their molecular refractivities.

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[1] *Wied. Ann.* **9**, 642 (1880); **11**, 77 (1880).

[2] *Journal de Phys.* 447 (1885).

[3] *Phil. Mag.* **27**, 141 (1889).

[4] *Amer. Chem. Journ.* **16**, 625 (1894) ; **17**, 473 (1895).

Relations between the Molecular Refractivities of Substances. — The relation between refractivity and composition has been carefully worked out by Landolt.[1] The following results are taken from his papers: —

		$\frac{M(n-1)}{d}$				$\frac{M(n-1)}{d}$	
Water,	H_2O	5.96		Methyl alcohol,	CH_4O	13.17	
			7.95				7.53
Formic acid,	CH_2O_2	13.91		Ethyl alcohol,	C_2H_6O	20.70	
			7.20				7.60
Acetic acid,	$C_2H_4O_2$	21.11		Propyl alcohol,	C_3H_8O	28.30	
			7.46				7.81
Propionic acid,	$C_3H_6O_2$	28.57		Butyl alcohol,	$C_4H_{10}O$	36.11	
			7.65				7.78
Butyric acid,	$C_4H_8O_2$	36.22		Amyl alcohol,	$C_5H_{12}O$	43.89	

		$\frac{M(n-1)}{d}$	
Ethyl formate,	$C_3H_6O_2$	29.80	
			6.36
Ethyl acetate,	$C_4H_8O_2$	36.16	
			2 × 7.58
Ethyl butyrate,	$C_6H_{12}O_2$	51.32	
			7.88
Ethyl valerate,	$C_7H_{14}O_2$	59.20	

Landolt concluded[2] from a large number of such data that the molecular refraction increases a nearly constant amount for the common difference in composition of CH_2. This increase is about 7.60.

In a similar manner, it was shown that the molecular refraction of two compounds which differ in composition by one carbon atom, is about 5. If they differ by two hydrogen atoms, the difference between their molecular refractions is 2.6. If they differ by an oxygen atom, the difference between their molecular refractions is about 3 units, and so on. The refraction equivalents of a number of the elements were thus worked out.

Landolt showed that the refraction equivalents of carbon, hydrogen, and oxygen, in their compounds, were almost exactly the same as the refraction equivalents in the free state. From the refraction equivalents of these elements he calculated the index of refraction of a number of compounds composed of carbon, hydrogen, and oxygen, and compared the results obtained with those found directly by experiment. A few of his results are given.

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[1] *Pogg. Ann.* **122**, 545 (1864); and **123**, 595 (1864).

[2] *Wied. Ann.* **123**, 611 (1864).

Take the case of ethyl alcohol C_2H_6O. The refraction equivalent of carbon is 5, that of hydrogen 1.3, and that of oxygen 3. The molecular refraction of ethyl alcohol would be calculated thus:—

$$2 \times 5 + 6 \times 1.3 + 1 \times 3 = 20.8.$$

The index of refraction of a compound, n, is calculated from the molecular refraction R, and the density D, as follows; P being the molecular weight:—

$$n = 1 + \frac{R}{P} D.$$

In an analogous manner Landolt calculated the indices of refraction of other substances.

	n Calculated	n Found
Methyl alcohol, CH_4O	1.328	1.328
Ethyl alcohol, C_2H_6O	1.362	1.361
Propyl alcohol, C_3H_8O	1.381	1.379
Formic acid, CH_2O_2	1.361	1.369
Acetic acid, $C_2H_4O_2$	1.371	1.370
Propionic acid, $C_3H_6O_2$	1.388	1.385
Methyl acetate, $C_3H_6O_2$	1.352	1.359
Ethyl acetate, $C_4H_8O_2$	1.373	1.371
Methyl butyrate, $C_5H_{10}O_2$	1.387	1.387
Methyl valerate, $C_6H_{12}O_2$	1.392	1.393
Aldehyde, C_2H_4O	1.326	1.330
Acetone, C_3H_6O	1.353	1.357

The close agreement between the index of refraction of a large number of compounds, calculated as described above, and as found experimentally, led Landolt to the conclusion that *the molecular refraction of a compound is the sum of the refraction equivalents of the elements which enter into the compound.*

Landolt[1] also compared the molecular refractions of a number of metameric substances.

		Molecular Refraction
Propionic acid	$C_3H_6O_2$	28.57
Methyl acetate		29.36
Ethyl formate		29.18
Butyric acid	$C_4H_8O_2$	36.22
Ethyl acetate		36.17
Valeric acid	$C_5H_{10}O_2$	44.05
Methyl butyrate		43.97

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[1] *Pogg. Ann.* **123**, 602 (1864).

The molecular refractions of metameric substances do not differ very considerably from one another. There are appreciable differences in some cases, but even these are not very great.

The effect of constitution on molecular refraction, while recognized by Landolt, was not carefully investigated by him.

Effect of Constitution on Refractivity. — The first systematic study of the effect of constitution on refractivity was made by Brühl.[1] Gladstone had found that the molecular refraction of a considerable number of certain classes of substances, as calculated from their composition, differed considerably from the value found experimentally. He observed that these compounds belonged to the benzene series, and then studied a large number of benzene derivatives. These showed, in general, a much higher refractivity than corresponded to their composition. These abnormally high results were evidently due to the presence of the benzene ring.

Brühl began the study of the effect of constitution on refractivity in 1878, and has continued his work on such problems up to the present. He found that carbon atoms united by "double union" had a greater influence on refractivity than singly united carbon. This is shown by the following results taken from the paper of Brühl. The saturated and corresponding unsaturated compound are given together.

	Molecular Refraction Observed	Molecular Refraction Calculated	Diff.
Allyl alcohol, C_3H_6O	28.00	27.80	0.2
Propyl alcohol, C_3H_8O	27.09	25.22	1.87
Propyl aldehyde, C_3H_6O	25.42	25.22	0.2
Acroleïne, C_3H_4O	25.31	22.64	2.67
Isobutyric acid, $C_4H_8O_2$	35.48	35.56	0.08
Methylacrylic acid, $C_4H_6O_2$	35.07	32.98	2.09

There is a difference between the calculated and observed molecular refraction of about 2 for the compounds containing one doubly united carbon atom; the refractivity being calculated from the composition.

Brühl also studied compounds containing two and three doubly united carbon atoms.[2]

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[1] *Lieb. Ann.* **200**, 139 (1880).

[2] *Ibid.* **200**, 139 (1880).

COMPOUNDS WITH TWO DOUBLY UNITED CARBON ATOMS

	MOLECULAR REFRACTION OBSERVED	MOLECULAR REFRACTION CALCULATED	DIFF.
Valerylene, C_5H_8	38.7	34.6	4.1
Diallyl, C_6H_{10}	46.0	42.1	3.9

Each double union corresponds in these substances to about 2 units.

The following compounds were supposed to contain three double unions: —

	MOLECULAR REFRACTION OBSERVED	MOLECULAR REFRACTION CALCULATED	DIFF.
Benzene, C_6H_6	42.2	36.9	5.3
Monochlorbenzene, C_6H_5Cl	50.7	45.1	5.6
Monobrombenzene, C_6H_5Br	55.8	50.4	5.4
Aniline, C_6H_7N	49.8	43.5	6.3

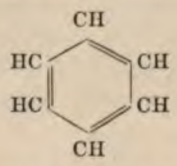
Here the three double unions correspond to about 6 units in the molecular refraction.

It thus seems that the presence of a double union between carbon atoms in a compound has a constant influence on its refractive power, and if there is more than one pair of doubly united carbon atoms, each double union has the same influence as if it alone were present.

The effect on refractivity of carbon atoms united by triple union, as in acetylene, was also studied. A pair of carbon atoms united by triple union raises the refractivity by 1.8 to 1.9 units. Carbon united by triple union has thus a slightly smaller influence than when united by double union.

Brühl points out at the close of this important paper that refractivity can be used to throw light on the constitution of compounds of carbon. If the question is to determine whether a given compound contains a doubly linked carbon atom, it is only necessary to determine its refractive power. If the refractivity determined experimentally agrees with that calculated from the composition of the molecule, on the assumption that all the carbon atoms are united by single union, then we can conclude that there are no doubly linked carbon atoms in the molecule. If the refractivity found is about two units higher than that calculated on the above assumption, then there is one double union in the molecule; if the refractivity found is about four units higher than that calculated, then there are two double unions in the molecule; and so on.

Constitution of Benzene.—This method was applied by Brühl to benzene. We have seen from results already given that the molecular refraction of benzene and its derivatives, as found experimentally, is nearly six units higher than the molecular refraction calculated on the assumption that the six carbon atoms are united by single unions. Since one double union increases the molecular refraction by two units, we must conclude that there are three double unions in the benzene molecule. We are thus led by the method of refractivity to the formula of benzene proposed by Kekulé:—



This represents the molecule of benzene as containing three singly and three doubly united carbon atoms, and on the whole is probably the most generally accepted formula for benzene which we have up to the present. It should, however, be stated here that another physical chemical method has led to exactly the opposite conclusion; viz. that in benzene we have all the carbon atoms united by single bonds. It is impossible to decide at present between these two conclusions, but the fact that such different results are obtained by different methods should make us cautious in accepting as final the results obtained by any one method, however reliable it apparently may be. Gladstone[1] again took up the study of refraction after Brühl[2] had published his earlier work, and sought to obtain further evidence in reference to the refraction-equivalents of carbon, hydrogen, oxygen, and nitrogen in organic compounds.[3] A large number of organic compounds were investigated, and the refraction-equivalents of a number of the elements determined. The refraction-equivalent of the CH_2 group was found to be 7.63. The refraction-equivalent of hydrogen is very close to 1.3. Therefore, the refraction-equivalent of carbon must be very nearly 5. In the aromatic hydrocarbons the refraction-equivalent of carbon is about 6. A still larger value was found for carbon among some of the higher members of homologous series of hydrocarbons. Gladstone also worked out the refraction-equivalents of a number of other elements. Chlorine was found to be 9.9, bromine 15.3, and iodine 24.5. Oxygen had been shown by Brühl to have two values,—a value of 3.4 when in the carbonyl condition, and of 2.8 when oxygen is united to two other atoms. Gladstone found the value 2.9. Nitrogen was found to have two values, 4.1 and 5.1 in different compounds. The lower value was found in the nitrates, and the higher in the organic bases and amides. The higher value, however, was found in the majority of cases.

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[1] *Journ. Chem. Soc.* **45**, 241 (1884).

[2] *Lieb. Ann.* **200**, 139 (1880); **203**, 1, 255, 363 (1880); *Men. Akad. Ber.* **11**, 84.

[3] *Proc. Roy. Soc.* 1881, 327.

This work of Gladstone shows conclusively the effect of constitution on refractivity, and thus confirms the conclusions of Brühl. In Gladstone's own words: "These optical properties seem capable of deciding with certainty whether an organic body is a saturated compound or not. They indicate also the number of carbon atoms in that condition which is generally denoted as 'doubly linked,' and they give us a clew as to the mode in which oxygen and nitrogen are combined."

In later investigations Brühl[1] pointed out even more clearly and conclusively the effect of constitution on refractivity. He laid down as the fundamental law of refraction, that the refractivity of carbon and hydrogen varies according to the way in which they are combined. For any given combination it is *approximately* constant, depending only slightly upon the configuration of the atoms in the different compounds. The monovalent elements have, on the other hand, nearly constant atomic refractions.

Brühl takes up again the question of the constitution of benzene as determined by its refractive power. The most accurate work gives a molecular refractivity of 25.93. The molecular refractivity calculated for the formula C_6H_6 is 21.12. The difference is 4.81. This corresponds to 3×1.60, which means that there are three ethylene groups in the benzene molecule, corresponding to the formula of Kekulé.

He then studied again the effect of the acetylene union $\begin{array}{c}C\\|||\\C\end{array}$ on refractivity, and found that it corresponded to 2.02. If in the formation of benzene from three molecules of actylene, the three triple unions were transformed into nine single unions, then the molecular refraction of liquid benzene should be about 6.06 smaller than that of three molecules of acetylene gas. The difference as found was only 1.19. Therefore, when acetylene passes into benzene the triple unions are not converted into single unions.

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[1] *Lieb. Ann.* **235**, 1 (1886); **236**, 233 (1886). *Ztschr. phys. Chem.* **1**, 307 (1887).

Brühl found, on the other hand, that when an acetylene union passes into an ethylene union there is a decrease in the refractivity of 0.40. When three acetylene unions pass into three ethylene unions, the decrease in refractivity would, therefore, be $0.40 \times 3 = 1.20$; and this is exactly the difference between the refractivity of three molecules of ethylene and the molecule of benzene formed from them. We are, therefore, led to the conclusion that when three molecules of acetylene form a molecule of benzene, the acetylene unions pass over into ethylene unions, thus:—

$$3\,HC\equiv CH = 3 - HC = CH -$$

which is the Kekulé formula for benzene.

The above line of reasoning is so clear and so satisfactorily confirmed by experimental evidence at every point, that there would seem to be no escape from the conclusion were it not for the conflicting result, which, as we shall see, is furnished by another physical chemical method.

Molecular Refraction in General an Additive Property. — As the final result, up to the present, which has been reached by the work of Gladstone and especially of Brühl, it can be stated that the molecular refraction of a compound is, in general, the sum of the atomic refractions of the atoms which enter into the molecule. This is only approximately true, since, as we have seen, constitution has a marked influence in some cases on refractivity. The atomic refraction is approximately constant under all conditions only for the univalent elements. Oxygen in the carbonyl condition has a greater refractive power than in the hydroxyl condition. The presence of double or triple bonds in the molecule increases its refractivity, as we have seen in ethylene, acetylene, and benzene. That constitution has a marked influence on the refractivity of other elements, especially nitrogen, has been shown by the work of Brühl[1] and others, but reference only can be made to these investigations.

Atomic Refractions of Some of the More Common Elements. — The atomic refractions of some of the best known elements are given in the following table. Column I is taken from the work of Brühl,[2] and is the refractivity referred to the red hydrogen line. Column II contains the results given by Conrady,[3] and are referred to the sodium line D.

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[1] *Ztschr. phys. Chem.* **16**, 193, 226, 497, 512 (1895); **22**, 373 (1897); **25**, 577 (1898). *Gazz. chim. ital.* **24**, I (1894) ; **25**, II (1895).

[2] *Ztschr. phys. Chem.* **7**, 191 (1891).

[3] *Ibid.* **3**, 210 (1889).

	COLUMN I RED HYDROGEN LINE	COLUMN II SODIUM LINE D
Carbon united by single bond	2.365	2.501
Hydrogen	1.103	1.051
Hydroxyl oxygen	1.506	1.521
Oxygen united as in ether	1.655	1.683
Carbonyl oxygen	2.328	2.287
Nitrogen united to carbon with one bond	2.760	——
Chlorine	6.014	5.998
Bromine	8.863	8.927
Iodine	13.808	14.120
Ethylene union (=)	1.836	1.707
Acetylene union (≡)	2.220	——

The atomic refractions of the elements of the first and second groups of the Periodic System have been determined by Kanannikoff.[1]

ROTATION OF THE PLANE OF POLARIZED LIGHT

Optically Active Substances. — It was known nearly a hundred years ago that when a beam of polarized light is passed through certain liquids, the plane of polarization is rotated or turned. This phenomenon was manifested by many substances in the crystalline condition, also by a number of carbon compounds in the liquid state and in solution. We are concerned here only with those optically active substances which are liquid at ordinary temperatures, or which are in solution. Some of the substances rotate the plane of polarization to the right and are called dextro-rotatory; others rotate to the left, and are termed lævo-rotatory. Dextro-rotation is indicated by the plus sign (+), lævo-rotation by the minus sign (−).

The number of substances whose rotatory power can be compared has increased enormously in the last few years. Biot and Seebeck pointed out in 1815 that certain organic substances have the power to rotate the plane of polarization. Oil of turpentine, and sugar and tartaric acid in aqueous solution, have this property, as was shown at this early date. From this time to 1879 the number of optically active substances increased to 300, while to-day we know over 700 substances[2] which have the power to rotate the plane of polarized light. The reason for the enormous activity in the preparation and study of these optically active substances will become apparent in the next few pages.

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[1] *Journ. prakt. Chem.* [2], **31**, 321 (1885).

[2] For further details consult the admirable book of Landolt: *Das optische Drehungsvermögen organischer Substanzen*, 2d edition, 1898.

Measurement of Rotation. — The instrument used in measuring the rotation of polarized light is known as the polarimeter. A beam of white light, or better, of monochromatic light, is passed through a Nicol's prism and polarized. This is then passed through a second Nicol's prism, which is turned until the light is completely extinguished. The position of the second prism or analyzer is then carefully noted. A glass tube containing the liquid to be investigated is then inserted in the path of the polarized ray of light, between the two Nicols. The plane of polarization is rotated and, consequently, the field of the second Nicol is no longer dark. It is now necessary to rotate the second Nicol, or analyzer, through a given angle to obtain again extinction of the light. The angle through which the analyzer must be rotated is read on the circular scale, and this is the angle through which the plane of polarization has been turned by the layer of the liquid used.

The rotatory power of a liquid depends chiefly upon the chemical nature of the substance, as we shall see. It evidently depends also upon the thickness of the column of liquid through which the polarized ray passes. It depends further upon the wave-length of light and upon the temperature. In measuring the rotatory power of a liquid all of these factors must be taken into account. The normal temperature chosen for such work is usually 20°. It is most convenient to use as monochromatic light that of the sodium flame.

Specific and Molecular Rotation. — Biot defined the specific rotation of an optically active liquid as that produced by a layer a decimetre in length, or if a solution it must contain one gram of the active substance in the volume of one cubic centimetre. But the density of the liquid must be taken into account. If we represent the specific gravity of the liquid by d, the length of the column of liquid expressed in decimetres by l, the rotation to the right or left expressed in degrees by α; the specific rotation A for a definite temperature (20°) and a definite wave-length of light (D light) is expressed thus:—

$$A = \frac{\alpha}{ld}.$$

This specific rotation is a characteristic constant for the compound in question.

In order to discover relations we must deal with comparable quantities of substances; and preferably with quantities which bear the same relations to one another as the molecular weights of the substances in question. If we deal with gram-molecular weights of substances, the observed rotation is known as the *molecular rotation.* The molecular rotation M is obtained by multiplying the specific rotation of the substance by the molecular weight m. Since the molecular rotation thus obtained is very high, it has been found convenient to divide this value by 100. The molecular rotation would then be calculated from the specific rotation as follows: —

$$M = \frac{m}{100} \frac{a}{ld}.$$

If we are dealing with a solution containing p grams of substance in a volume of v cubic centimetres of solution, and l is the length of the column in decimetres, the specific rotation is expressed thus: —

$$A = \frac{av}{lp},$$

the molecular rotation thus: —

$$M = \frac{m}{100} \frac{av}{lp}.$$

Optical Activity and Chemical Constitution. — The earlier work in this field had to do with the discovery of compounds which are optically active. The discovery of any relation between optical activity and chemical composition and constitution belongs to a later period. Pasteur[1] threw much light on this problem by his discovery that ordinary racemic acid can be broken down into two modifications, the one turning the plane of polarization to the right, the other to the left. If a solution of sodium ammonium racemate is evaporated at low temperatures, rhombic, hemihedral crystals separate, having the composition $Na.NH_4.C_4H_4O_6 + 4\,H_2O$. The crystals are, however, not all identical. The tetrahedral faces on some of the crystals are different from those on other crystals. Indeed, the crystals divided themselves sharply into two classes, the one containing dextro-hemihedral faces, the other lævo-hemihedral faces. We have here enantiamorphism, as in the case of quartz, the one crystal being the image of the other in a mirror.

The two kinds of crystals were separated mechanically, and dissolved in water. The solution containing the crystals with the right-handed faces rotated the plane of polarized light to the right; those with the left-handed faces rotated the plane of polarization to the left. In Pasteur's own words:[1] "When I had discovered the hemihedrism of all the tartrates, I quickly studied with care the double paratartrate (racemate) of sodium and ammonium. But I saw that the little tetrahedral faces, corresponding to those of the isomorphous tartrates, were placed relative to the principal faces of the crystal, sometimes on the right, at other times on the left, on the different crystals which I have obtained. If these faces were respectively prolonged, they would give the two symmetrical tetrahedra of which we have spoken. I carefully separated the right-handed from the left-handed hemihedral crystals. I observed separately their solutions in the polarizing apparatus of Biot, and saw with surprise and delight that the right-handed hemihedral crystals rotated the plane of polarization to the right, and that the left-handed crystals rotated to the left. . . . The rotatory power thus shows the kind of asymmetry of the crystals. The two kinds of crystals are isomorphous, and isomorphous with the corresponding tartrate, but the isomorphism presents itself here with a peculiarity thus far not exemplified; this is the isomorphism of two asymmetric crystals, the one being the image of the other in a mirror."

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[1] *Ann. Chim. Phys.* [3], **24**, 442 (1848); **28**, 56 (1850); **31**, 67 (1851).

In a later investigation, Pasteur[2] decomposed the two salts obtained from racemic acid, and secured the two corresponding acids, which he termed dextro-racemic and lævo-racemic acids. The dextro-racemic acid was shown to be identical with ordinary dextro-tartaric acid, rotating the plane of polarization to the right. The lævo-racemic acid rotated the plane of polarization just as much to the left, as the dextro to the right. From racemic acid Pasteur was thus able to obtain two acids, the one rotating the plane of polarization to the right, the other to the left; the racemic acid itself being optically neutral. He was, however, not content to stop here. If racemic acid had been broken down into two optically active constituents, then, when these constituents were brought together in the proper proportion, racemic acid should be reformed. Pasteur mixed concentrated solutions of dextro-racemic and lævo-racemic acids. Heat was evolved, and crystals of racemic acid separated in abundance. Instead of dextro-racemic, ordinary dextro-tartaric, acid could be used, since the two are identical.

In this way an optically inactive substance was, for the first time, broken down into two optically active substances, which rotated the plane of polarized light to the same extent, but in the opposite direction. Further, the optically inactive substance was formed again by mixing solutions of the two optically active substances. From these results Pasteur reasoned as follows:[1] "Are the atoms of the dextro acid grouped in the form of a right-handed spiral, or do they stand at the corners of an irregular tetrahedron, or do they exist in some other asymmetric arrangement? We are not able to answer these questions. But there is no doubt on this point, that an asymmetric grouping of the atoms, corresponding to an object and its image in a mirror, must be present. It is just as certain that the atoms of the lævo acid have exactly the opposite arrangement. We know, finally, that racemic acid is formed by the union of these two oppositely asymmetric atomic groupings."

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[1] *Ann. Chim. Phys.* [2], **24**, 456. [2] *Ibid.* [3], **28**, 56 (1850).

The most important advance of a general character, which was introduced by this work of Pasteur, was the clear recognition of *molecular asymmetry* in the structure of chemical molecules. He was not able to point out the nature of this asymmetry, since the facts known at that time in reference to the constitution of optically active substances were far too meagre to lead to any wide-reaching generalization.

Theory of Van't Hoff and Le Bel. — In the period following that in which the work of Pasteur was done, much light was thrown on the constitution of chemical compounds, and especially upon the constitution of organic compounds. With this newly acquired knowledge Van't Hoff in Holland and Le Bel in France were able to connect optical activity with chemical constitution. Van't Hoff's paper in Dutch bears the date Sept. 5, 1874. Le Bel's paper[2] in French appeared in November, 1874. Since Le Bel did not go as far as Van't Hoff in advancing a definite theory, his contribution to this important subject will be taken up first.[3]

Le Bel fully recognized, from the work of Pasteur, the importance of asymmetry in conditioning rotatory power. "If the asymmetry exists only in the crystalline molecule, only the crystal will be active; if, on the contrary, it belongs to the chemical molecule, the solution of the substance will show rotatory power." Since the latter is the case, we must regard the chemical molecule as asymmetric. This was the starting-point for Le Bel. In compounds containing carbon the cause of the asymmetry is to be ascribed to the presence of a carbon atom combined with four different atoms or groups. Le Bel illustrates this principle by means of optically active substances known at that time, and shows by a number of examples that optically active compounds contain an asymmetric carbon atom, *i.e.* a carbon atom in combination with four different atoms or groups. The simplest example is lactic acid, which contains an asymmetric carbon atom in combination with hydrogen, hydroxyl, methyl, and carboxyl, thus: —

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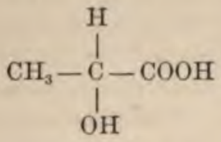
[1] *Recherches sur la dissymétrie moléculaire*, p. 25.

[2] *Bull. Soc. Chim.* [2], **22**, 337 (1874).

[3] "Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolutions." *Ibid.*



$$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-COOH$$

Le Bel pointed out at the very close of his important paper, that we never obtain by direct synthesis the dextro or the lævo acid, but always the inactive or racemic modification, which is a combination of equal parts of the two active forms.

Van't Hoff[1] also pointed out that in every optically active substance there is at least one carbon atom in combination with four different atoms or groups — one asymmetric carbon atom. This holds good up to the present, with the possible exception of one compound, which, according to Baeyer, is optically active and does not contain an asymmetric carbon atom. The compound in question is so complex that its constitution cannot be regarded as finally established, and it may yet be shown not to be an exception to the above generalization.

Van't Hoff, however, went much farther than simply to recognize asymmetry as the cause of optical activity. He attempted to point out the geometrical configuration which is probably fundamental to carbon compounds. Take the simplest saturated compound of carbon and hydrogen, CH_4. This substance had been shown by the work of Henry to be symmetrical; *i.e.* every hydrogen atom bears exactly the same relation to the molecule. By what geometrical configuration in three dimensions could this fact be represented? Plainly only by one, — the regular tetrahedron. The carbon atom is situated at the centre of such a tetrahedron, and the four hydrogen atoms at the four solid angles. Such an arrangement is symmetrical, and accords with all of the facts known in connection with the compound CH_4. In this way arose the theory of "*the tetrahedral carbon atom.*"

In every optically active substance, as we have seen, there is a carbon atom in combination with four different atoms or groups.

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[1] *La Chimie dans l'Espace.* Rotterdam, 1875.

The carbon atom is situated at the centre of the tetrahedron, and the four atoms or groups in combination with it are at the four solid angles of the tetrahedron. This arrangement is, of course, asymmetric, and thus we have the theory of "*the asymmetric tetrahedral carbon atom.*"

These simple suggestions lie at the foundation of all *stereochemistry*, which is one of the most interesting and important phases of organic chemistry during the last quarter of a century. We can see at once, by means of the tetrahedron, why it is necessary that all the four atoms or groups in combination with the central carbon atom should be different. If any two atoms or groups are the same, it is impossible to construct two tetrahedra which cannot be superimposed. This can readily be seen by means of models. If, on the other hand, all four atoms or groups are different, then two tetrahedra containing these atoms or groups arranged around a central carbon atom, will always bear the relation to one another of an object and its image in a mirror. The two tetrahedra would represent enantiomorphous forms, and if one would rotate the plane of polarization to the right, the other would rotate it to the left. The theory thus explains why it is necessary to have all four of the atoms or groups around the central carbon atom different, in order to have optical activity.

The theory also explains the very important fact pointed out by Le Bel, that by synthesis we never obtain the dextro or the lævo form alone, but always a mixture of both forms. Since optical activity depends only on the arrangement of the constituents in the molecule, from the law of probability we would have just as many molecules formed having the one configuration as the other. For every dextro-rotatory substance there would thus be an equal quantity of the corresponding lævo compound formed. Here, again, the theory furnishes a satisfactory explanation of facts which, without its aid, are entirely inexplicable.

The presence of an asymmetric carbon atom is necessary, as we have seen, for optical activity. The converse does not hold true. We may have asymmetric carbon atoms present, and yet the compound be optically inactive. This fact is also satisfactorily explained by our theory. The compound may have more than one asymmetric carbon atom, as in inactive tartaric acid,[1] and the asymmetric carbon atoms may equalize each other's influence.

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[1] Inactive tartaric acid is a fourth modification of tartaric acid, and is to be distinguished from dextro-tartaric acid on the one hand, and from lævo on the other, and from racemic acid, a mixture of these two.

COOH.H.OH.C – C.OH.H.COOH.

This compound is optically inactive and cannot be broken down into optically active substances. The influence of the one carbon atom on polarized light is exactly equal and opposite to the influence exerted by the other, hence inactivity. Again, the compound may be optically inactive because it is composed of an equimolecular mixture or a dextro and a lævo substance. This, as we have seen, is the case with racemic acid; it is a mixture of equal parts of dextro and of lævo tartaric acid. Indeed, we never obtain one active substance directly by synthesis. The two optically opposite varieties are always formed together, and the mixture of these two, or the racemic modification, is the result. We have already seen in one case how it is possible to obtain optically active varieties from a racemic mixture; we will now examine more closely the methods available for separating racemic modifications into their optically active constituents.

Separation of Optically Active Isomeres from Racemic Modifications. — The synthesis of racemic modifications, or mixtures of equal quantities of dextro and lævo forms, is comparatively simple in many cases, and a large number of such syntheses have been effected. It then remains to separate the optically active isomeres from this mixture. Several methods have been used: —

I. We have seen how Pasteur made use of one method, viz. that based on the different crystalline forms of salts of the two active substances. He was able to separate the crystals mechanically, and from racemic acid to obtain dextro and lævo tartaric acid.

II. A second method consists in adding to the mixture of the isomeric components an optically active substance which will combine with them. The two compounds formed may differ sufficiently in properties to enable them to be separated. They may differ in solubility, crystal form, vapor tension, melting-point, etc. By utilizing some such differences a number of racemic forms have been separated into their constituents. The active alkaloids have proved very useful in this connection. Pasteur succeeded in separating racemic acid into dextro and lævo tartaric acids, by means of certain active alkaloids. The separation was effected through the difference in crystal form of the two compounds with the alkaloid. The free tartaric acids were easily obtained from the compounds with the alkaloids.

III. A third method of separating the constituents from a racemic modification consists in treating the mixture with certain organic forms. These will often destroy one of the active modifications in the mixture and leave the other. Thus, penicillium, allowed to act on a dilute solution of ammonium racemate, will destroy the dextrorotatory compound and leave the lævo-rotatory. In this way, of course, only one of the active modifications can be obtained, the other having been destroyed by the organism.

By means of these methods of separating racemic mixtures into optically active constituents, and of chemical synthesis, we can prepare optically active substances in the laboratory, and a large number of such compounds have already been prepared. The claim of Pasteur that optically active substances can be made only through the agency of the life process, does not seem to be borne out by the facts. In his later claim,[1] in reply to a criticism of his view by Schützenberger, he says: "*To transform an inactive substance into another inactive substance* which can be resolved simultaneously into a dextro substance and its corresponding laevo compound, is not at all comparable with the possibility of transforming *an inactive substance into a simple active substance.*" Here again the view of Pasteur does not find general support. That active substances can be made in the laboratory, without the intervention of life, is just as certain as that organic compounds can be synthesized from dead matter without the intervention of the life process.

The theory of Van't Hoff and Le Bel has proved most fruitful in throwing light on many cases of isomerism, which, without its aid, are entirely inexplicable. It has also suggested many new lines of work, and has probably contributed more to the advancement of organic chemistry in recent times, than any other line of thought. We need only refer to the work of such men as Wislicenus,[2] Hantzsch and Werner, V. Meyer and Auwers, and Emil Fischer, to show what a tremendous influence this theory of the tetrahedral carbon atom has had.

The Hypothesis of Guye. — The theory of the asymmetric carbon atom as the cause of optical activity has been tested quantitatively by Guye.[3] He attempted to discover relations between the nature and magnitude of the rotation, and the nature of the atoms or groups which are combined with the carbon atom and occupy the corners of the tetrahedron.

If we assume that the four valences of carbon are directed toward the four solid angles of a regular tetrahedron, the six planes of symmetry of the compound CR_4 represent what Guye termed the *planes of symmetry of carbon.* When the carbon is symmetrical, the centre of gravity of the molecule will lie in at least one of the six planes of symmetry. When the carbon is asymmetrical, the centre of gravity will not lie in any of these planes. If we represent the distances from the centre of gravity of the molecule to each of the planes of symmetry by d_1, d_2, d_3, d_4, d_5, d_6, respectively, the product of these six values is known as the *product of asymmetry*. This product is zero when the carbon is symmetrical, but has different values as the asymmetry differs. If these differences are regarded as positive or negative, depending on the side of each plane on which they occur, the product of asymmetry will be positive or negative, as the number of negative factors is even or odd.

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[1] *Compt. rend.* **81**, 128 (1875).

[2] *Ueber die Räumliche Anordnung der Atome in organischen Molekulen.*

[3] *Compt. rend.* **110**, 714 (1890).

The hypothesis advanced by Guye is, in his own words: "The product of asymmetry can then serve as a measure of the asymmetry of the carbon, and it is but natural to suppose that the rotatory power undergoes the same variation as this product."

Guye then deduces certain consequences of this hypothesis which can be tested experimentally:—

I. Whenever an element or group is substituted by another, and the centre of gravity of the molecule remains on the same sides of the planes of symmetry of the carbon, the rotatory power should preserve the same sign.

II. If by the substitution the centre of gravity of the molecule is removed farther from the planes of symmetry, the rotatory power should be increased. If, on the contrary, the centre of gravity approaches more nearly the planes of symmetry, the rotatory power should decrease.

III. If by the substitution the centre of gravity is replaced from one side of one of the planes of symmetry to the other, the rotatory power should undergo a change in sign.

The remainder of Guye's first paper is devoted to the discussion of experiments which verified these three principles. By varying the masses of the atoms or groups in combination with carbon, he could vary the position of the centre of gravity of the molecule. By increasing the mass of the group which replaces the hydrogen of the carboxyl in some organic acid, the centre of gravity could be removed farther from the principal planes of symmetry. The rotatory power should be increased by this means. The following results were obtained with tartaric acid:—

	Rotation
Methyl tartrate	+ 2.14
Ethyl tartrate	+ 7.66
Propyl tartrate	+ 12.44
Isobutyl tartrate	+ 19.87

If in dextro-tartaric acid each of the two hydroxyl hydrogen atoms is replaced by benzoyl, we have a group of mass 17 substituted by a group of mass 121. The centre of gravity will pass from one side to the other of a plane of symmetry. Consequently, dibenzoyl-tartaric acid should be laevo-rotatory. Its rotation is -117.68.

If we now replace the hydrogen of dibenzoyl tartaric acid by the groups methyl, ethyl, propyl, butyl, the centre of gravity of the molecule will lie on the same side of the plane of symmetry as in the acid itself. But it will approach the plane of symmetry as the substituting group becomes heavier and heavier, and, consequently, the amount of the lævo rotation should become less and less as the group which replaces the hydrogen becomes of greater mass. The facts accord with the hypothesis.

	Rotation
Methyldibenzoyl tartrate	-88.78
Ethyldibenzoyl tartrate	-60.02
Isobutyldibenzoyl tartrate	-41.95

Since this hypothesis was proposed, Guye has carried out many and elaborate investigations[1] to test its validity. The result of all this work is to show that the hypothesis accords with the facts in many directions. But it is only a partial expression of the truth. It alone is not sufficient to account for optical activity. In addition to the effect of mass on optical activity, we must take into account the relative position of the four groups, their mutual action on one another, their configuration, and the chemical nature of the atoms themselves which are combined with the carbon atom. The phenomenon of optical activity is, then, far more complicated than would appear from the hypothesis of Guye alone. This hypothesis is undoubtedly a step in the right direction toward the solution of the problem of optical activity in terms of molecular composition and molecular structure, but it is only a step, and by no means the last one.

MAGNETIC ROTATION OF THE PLANE OF POLARIZATION

Observation of Faraday. — The observation was made by Faraday[2] that many substances acquire the power of rotating the plane of polarization when placed in a magnetic field. He first worked with glass, but soon discovered that other substances possess the same power of becoming active under the influence of magnetic force. If the substance has a rotatory power of its own, as oil of turpentine, sugar, tartaric acid, etc., the effect of the magnetic force is to add to or subtract from their specific power, according as the natural and acquired rotatory powers have the same or different signs. Faraday found that substances having very different chemical, physical, and mechanical properties become optically active under the magnetic influence. His work included solids and liquids, acids, alkalies, and neutral substances. He worked with solutions in alcohol and in water, and of the latter class he studied some 150 examples. He found that the "exceeding diversity of substance caused no exception to the general result, for all the bodies showed the property."

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[1] *Compt. rend.* **111**, 745; **114**, 473; **116**, 1133, 1378, 1451, 1454; **119**, 906; **120**, 157, 452, 632, 1274 (1890–1895). *Ann. Chim. Phys.* [6], **25**, 145 (1892). Guye and Chavanne: *Compt. rend.* **116**, 1454; **119**, 906.

[2] *Phil. Trans.* **136**, 1 (1846). *Pogg. Ann.* **68**, 105 (1846).

Investigation of De La Rive. — An investigation of the magnetic rotatory power of substances was published by De La Rive[1] in 1871. He determined the magnetic rotatory power of substances, in terms of water as unity, and found that the magnetic rotatory power does not have any relation to other physical properties. Rise in temperature diminished the rotatory power of liquids. The rotatory power of a mixture of two liquids is the mean of the rotatory powers of the constituents, when the two liquids do not act chemically.

Work of Becquerel. — An elaborate investigation on magnetic rotatory power was carried out in 1877, by Becquerel.[2] He studied also the refractive power of substances, and discovered certain relations between the two properties. For the substances of a given chemical family the magnetic rotation divided by the term $n^2\ (n^2-1)$, n being the index of refraction, is very nearly a constant. Becquerel studied the effect of the chemical nature of the substance on magnetic rotatory power, and concluded that the chemical nature of substances affects directly their magnetic rotatory power, and the different elements combined in a compound exert their own independent influence.

Investigations of Perkin. — The most elaborate investigations, by far, in the field of magnetic rotation, are those of Perkin. His work was begun[3] more than fifteen years ago, and has been continued nearly up to the present.[4] Perkin has investigated especially the relations between chemical composition and constitution, and magnetic rotation. He took the molecular rotatory power of water as unity, and compared the rotatory power of other substances with

[1] *Ann. Chim. Phys.* [4], **22**, 5 (1871).

[2] *Ibid.* [5], **12**, 5 (1877).

[3] *Journ. prakt. Chem.* [2], **31**, 481 (1885); [2], **32**, 523 (1885).

[4] *Journ. Chem. Soc.* **49**, 777; **51**, 808; **53**, 561, 695; **59**, 981; **61**, 287, 800; **63**, 57; **65**, 402, 815; **67**, 255; **69**, 1025 (1880–1896).

it. Similarly, the specific rotatory power of a substance is its specific rotation referred to that of water under exactly the same conditions.

A few of the results obtained by Perkin will show what relations were discovered by him. Take first the influence of the CH_2 group, obtained by studying homologous series of compounds.

	MOLECULAR MAGNETIC ROTATION.	DIFF.
Formic acid	1.617	
Acetic acid	2.525	0.908
Propionic acid	3.462	0.937
Butyric acid	4.472	1.010
Methyl bromide	4.644	
Ethyl bromide	5.851	1.207
Propyl bromide	6.885	1.034
Methyl iodide	9.009	
Ethyl iodide	10.075	1.066
Propyl iodide	11.080	1.005

There is thus very nearly a constant difference in the molecular magnetic rotation produced by the constant difference in composition of CH_2, where the compounds have similar constitution. This difference is about 1.02. The effect of constitution on magnetic rotation can best be seen by studying isomeric substances.

	MOLEC. MAG. ROTATION		MOLEC. MAG. ROTATION
Propyl alcohol	3.768	Propyl chloride	5.056
Isopropyl alcohol	4.019	Isopropyl chloride	5.159
Propyl bromide	6.885	Butyric acid	4.472
Isopropyl bromide	7.003	Isobutyric acid	4.479

These results show that constitution has a marked influence on magnetic rotation, and has a different influence in compounds of different composition. Perkin has attempted to throw light on a number of interesting questions by means of the magnetic rotation method, but for further details in this connection his original papers must be consulted.

Work of Rodger and Watson. — The section on magnetic rotation should not be closed without brief reference to the work of Rodger and Watson.[1] They used a stronger magnetic field and, consequently, had a larger rotation to measure. Their work consists chiefly in improving the apparatus to be used in studying magnetic rotation. A few results were obtained, and it is to be hoped that further work will be done with the stronger field.

MAGNETIC PROPERTY

Paramagnetic and Diamagnetic Bodies. — Faraday[2] found that substances in general divide themselves into two classes with respect to their behavior toward a magnet. Those which were attracted by the magnet, such as iron, cobalt, nickel, manganese, chromium, platinum, etc., were termed paramagnetic. Those which were repelled by the magnet, such as bismuth, tin, mercury, copper, arsenic, iridium, uranium, tungsten, etc., were called diamagnetic.

The magnitude of the attractive and repellent forces was measured by Plücker.[3] He found that the magnitude of the attractive force was proportional to the number of magnetic molecules present.

Work of Wiedemann. — The most accurate work which has been done on the magnetic properties of substances is that of G. Wiedemann.[4] He measured the force by means of the torsion of a German silver wire. The specific magnetic attraction, μ, is expressed thus: —

$$\mu = \frac{A}{BC^2},$$

where A is the attraction exerted, B, the mass of the substance, and C, the magnetism of the electromagnet. The molecular magnetism, M, is the specific magnetism, μ, multiplied by the molecular weight of the substance, m: —

$$M = m\mu.$$

Wiedemann confirmed the conclusion of Plücker, that the magnetic attraction is proportional to the number of molecules of dissolved salt. He also used different salts of the same metal, and found that the molecular magnetic attraction was the same for the different salts, if the magnetic metal was in the same state of oxidation in all of the salts.

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[1] *Ztschr. phys. Chem.* **19**, 323 (1896). *Phil. Trans.* **186** (A), 621 (1895).

[2] *Phil. Trans.* 1846, 1. *Pogg. Ann.* **69**, 289 (1846).

[3] *Pogg. Ann.* **74**, 321 (1848).

[4] *Ibid.* **126**, 1 (1865); **135**, 177 (1868). *Wied. Ann.* **32**, 452 (1887).

More Recent Work. — Henrichsen, working in part with Wleügel,[1] and in part alone,[2] has carried out a number of measurements on the magnetic property of substances. He has somewhat modified the torsion method of Wiedemann, and has used a number of diamagnetic substances. According to him, molecular magnetic repulsion, at least, is an additive property; being approximately the sum of the atomic repulsions. Certain constitutive influences manifest themselves; the presence of doubly united carbon seemed to increase the diamagnetic property.

Certain very simple relations between the atomic magnetic attractions of nickel, cobalt, iron, and manganese, as shown by aqueous solutions of their compounds, have been pointed out by Jäger and Stefan Meyer.[3] Their meaning is not at all apparent.

Meyer[4] has published a number of papers quite recently on various phases of this subject. In his most recent communication he concludes that when contraction in volume takes place in compounds, the paramagnetism increases; when dilation occurs, diamagnetism increases.

SPECIFIC GRAVITY AND VOLUME RELATIONS OF LIQUIDS

Specific Gravity, Specific Volume, and Molecular Volume. — By the specific gravity of a substance is meant the mass contained in a given volume. We must choose some substance as the unit and compare other substances with it. Water is usually taken as the unit. By specific volume of a substance is understood the volume in cubic centimetres occupied by a gram of the substance. If we represent the specific gravity of a substance by s, the specific volume is equal to $\frac{1}{s}$. The molecular volume M is the specific volume multiplied by the molecular weight m of the substance: —

$$M = \frac{m}{s}.$$

Methods of determining the Specific Gravity of Liquids. — A method for determining the specific gravity of a liquid consists in weighing a solid of known volume in the liquid by means of the Mohr balance, and determining the loss in the weight of the solid. This is exactly equal to the weight of liquid displaced by it. Knowing the volume of the solid immersed in the liquid, we know the volume of the liquid displaced by the solid. A more convenient method for determining the specific gravity of a liquid consists in weighing directly a known volume of the liquid. A number of forms of vessels have been devised for determining the specific gravity of liquids. That shown in Fig. 12 is the Ostwald modification of the Sprengel pycnometer.

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[1] *Wied. Ann.* **22**, 121 (1884).

[2] *Ibid.* **34**, 180 (1888).

[3] *Ibid.* **63**, 83 (1897).

[4] *Ibid.* **69**, 236 (1899); **68**, 325 (1899).

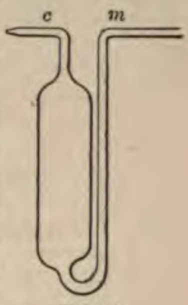

FIG. 12.

The liquid is drawn into the pycnometer through the capillary, *c*. The apparatus is then placed in a constant temperature bath and brought to the temperature desired. The liquid is brought to the mark at *m* by removing liquid from, or adding liquid to, *c*. The pycnometer is weighed empty; it is then filled with water and weighed, and finally filled with the liquid in question and reweighed. Let these weights be w_1, w_2, and w_3. If the weight of the displaced air is Δ, and we represent the specific gravity of the liquid by S—

$$S = \frac{w_3 - w_1 + \Delta}{w_2 - w_1 + \Delta}.$$

Work of Kopp.—Relations between the molecular volumes of certain liquids were early pointed out by Kopp.[1] He found that constant differences in composition corresponded to constant differences in the molecular volumes. Thus, the molecular volume of an ethyl compound is 234 units greater than that of the corresponding methyl compound. The atomic volumes of a number of the elements were worked out by Kopp, and it was shown that molecular volumes are approximately the sum of the atomic volumes of the elements present in the molecule.

Kopp's later investigations[2] confirmed, in the main, the results of his earlier work. Take homologous series of compounds:—

	MOLECULAR VOLUME	DIFFERENCE
Formic acid, CH_2O_2	41.8	21.7
Acetic acid, $C_2H_4O_2$	63.5	21.9
Propionic acid, $C_3H_6O_2$	85.4	21.2
Butyric acid, $C_4H_8O_2$	106.6	23.7
Valeric acid, $C_5H_{10}O_2$	130.3	
Ethyl formate, $C_3H_6O_2$	85.4	22.2
Ethyl acetate, $C_4H_8O_2$	107.6	18.2
Ethyl propionate, $C_5H_{10}O_2$	125.8	23.3
Ethyl butyrate, $C_6H_{12}O_2$	149.1	

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[1] *Lieb. Ann.* **41**, 79 (1842).

[2] *Ibid.* **96**, 153, 303 (1855).

A constant difference in composition corresponds to a constant difference in molecular volume.

The effect of constitution on molecular volume can be seen by studying isomeric substances.[1]

	Molecular Volume.
Acetic acid, $C_2H_4O_2$	63.6
Methyl formate, $C_2H_4O_2$	63.4
Ethyl valerate, $C_7H_{14}O_2$	173.5
Amyl acetate, $C_7H_{14}O_2$	173.4
Propionic acid, $C_3H_6O_2$	85.4
Ethyl formate, $C_3H_6O_2$	85.3
Methyl acetate, $C_3H_6O_2$	84.8

Isomeric substances have the same specific volumes. It should be observed that these determinations were made at the boiling-points of the liquids in question. Kopp[2] also found that two atoms of hydrogen and one atom of oxygen can replace one another without changing the molecular volume. Similarly, one atom of carbon and two atoms of hydrogen can replace each other without affecting the molecular volume. He calculated the atomic volume of carbon to be 11, of hydrogen 5.5, of carbonyl oxygen 12.2, and of hydroxyl oxygen 7.8. From these values Kopp calculated the molecular volumes of a large number of liquids, and showed that they agree very closely with the values found experimentally at the boiling-points of the substances.

More Recent Work. — That constitution has an influence on molecular volume is made probable by the more recent work. Buff[3] thought that carbon had a larger atomic volume in the unsaturated than in the saturated condition. Thorpe found that isomeric substances have approximately, but not exactly, the same molecular volumes at their boiling-points.

The conclusion from the best work which has been done is that molecular volumes are, in general, additive, — the sum of the atomic volumes. The effect of constitution, however, manifests itself especially with carbon and oxygen and, consequently, the law of Kopp that constant differences in composition produce equal differences in molecular volume is only an approximation to the truth.

VISCOSITY OF LIQUIDS

Methods of determining Viscosity. — The methods of determining the inner friction of a liquid, or its viscosity, are based upon two principles. Either a solid body is moved in the liquid and the resistance to the movement measured, or the liquid is moved over a solid, as through a capillary tube. The best methods are based upon the second principle. Definite volumes of liquids are allowed to flow through a capillary tube, and the time required is noted. The form of apparatus[1] consists of a bulb attached to a capillary tube, and a bulb or some other form of vessel at the other end of the capillary to receive the liquid. The volume of the first bulb is known, and the time required for this volume of the liquid to flow through the capillary is determined.

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[1] *Lieb. Ann.* **96**, 171 (1855). [2] *Loc. cit.* 172. [3] *Lieb. Ann. Suppl.* **4**, 129 (1865).

Work of Thorpe and Rodger. — The most elaborate, and probably the most accurate work which has ever been done on the viscosity of liquids, is that of Thorpe and Rodger.[2] These authors review the work which had already been done on viscosity, and then discuss their own. The aim of their investigation was to throw light on the relation between the viscosity of homogeneous liquids and their chemical nature. The method was to measure the time required by a liquid to flow through a capillary tube. The viscosity could be measured from zero up to the boiling-point of the liquid. The formula of Slotte was used for calculating viscosity: —

$$\eta = c(1 + bt)\,u.$$

η is the coefficient of viscosity in dynes per square centimetre; c, b, and u are constants, varying with the nature of the liquid. The viscosities of some seventy liquids were measured at different temperatures. To discover quantitative relations between viscosity and chemical nature, some temperatures must be chosen at which the liquids are in comparable condition with respect to their viscosities. Comparisons were made at the boiling-points of the liquids, but it was found better to use temperatures at which the rate of change of the viscosity coefficient is the same for all liquids — temperatures of equal slope.

Comparisons were, therefore, made at temperatures at which $\frac{d\eta}{dt}$ is the same for the different liquids. In all homologous series, except the alcohols, acids, and dichlorides, the group CH_2 increases the viscosity coefficient. Its influence diminishes as the series ascends. The compound with the highest molecular weight has the highest coefficient, among corresponding compounds. An iso-compound has always a larger coefficient than a normal compound.

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[1] *Ztschr. phys. Chem.* **1**, 285 (1887).

[2] *Proc. Roy. Soc.* 1894. *Jour. Chem. Soc.* **71**, 360 (1897). *Chem. News*, **69**, 123, 135 (1894). *Ztschr. phys. Chem.* **14**, 361 (1894).

Alcohols and acids give exceptional results. Constitution has a marked influence on the viscosity coefficient, as is shown by comparing saturated and unsaturated compounds.

If we compare molecular viscosities at equal slope, we find that for most substances these can be calculated from the constants for the atoms in the molecule. Some of these constants are:—

	VISCOSITY CONSTANTS
Hydrogen	44.5
Carbon	31.0
Hydroxyl oxygen	166.0
Carbonyl oxygen	198.0
Chlorine in monochlorides	256.0
Bromine in monobromides	374.0
Iodine in monoiodides	499.0
Double linkage	48.0
Ring grouping	244.0

The effect of constitution on viscosity is shown by the large value of the constant for ring-grouping, double linkage, etc., and for the different values of oxygen when in the hydroxyl and carbonyl condition. Water and the alcohols present marked exceptions to any relation thus far discovered between viscosity and chemical nature.

SURFACE-TENSION OF LIQUIDS

Surface-tension. Method of Measuring. — While gases tend to expand and increase their volume, the surface of a liquid tends to contract and occupy a smaller volume. This potential energy, present at the surface of liquids, produces a tension which is known as surface-tension. Any force which tends to increase the size of the liquid surface is opposed by the surface-tension of the liquid.

There are a number of methods of measuring the surface-tension of liquids, but of these the most convenient and important from the physical chemical standpoint is the so-called capillary method. The height to which the liquid rises in a capillary tube is determined, and from this the surface-tension of the liquid is calculated as follows: Let h be the height to which the liquid rises in a capillary tube of radius r, D the density of the liquid and d the density of the gas in which the experiment is carried out, and g the acceleration of gravity; the surface-tension T is obtained from these values:—

$$T = \tfrac{1}{2}\, ghr\,(D - d) \text{ (dynes per cm.).}$$

Relations between Surface-tension and Composition. — Relations between surface-tension and composition were pointed out in 1860 by Mendeléeff,[1] but more extended investigations were published in 1864 by Wilhelmy.[2] He compared the capillarity coefficients of substances, which he termed α. This was obtained from the constant A^2, by multiplying by S, the specific gravity of the liquid, and dividing by 2:—

$$\alpha = \frac{A^2S}{2}.$$

Wilhelmy found that an increase in composition of CH_2 does not appreciably change the value of α:—

	α
Methyl alcohol	2.42
Ethyl alcohol	2.32
Amyl alcohol	2.43

Addition of carbon increases the value of α:—

	α
Alcohol, C_2H_6O	2.36
Acetone, C_3H_6O	2.45
Amylene, C_5H_{10}	1.75
Xylene, C_8H_{10}	2.75

Addition of oxygen increases the coefficient:—

	α
Acetone, C_3H_6O	2.45
Ethyl formate, $C_3H_6O_2$	2.63
Lactic acid, $C_3H_6O_3$	3.94

Isomeric compounds have equal coefficients only when they have similar constitution:—

	α
Ethyl formate, $C_3H_6O_2$	2.63
Methyl acetate, $C_3H_6O_2$	2.58
Ethyl butyrate, $C_6H_{12}O_2$	2.55
Amyl formate, $C_6H_{12}O_2$	2.61

An extensive investigation on the capillary constants of liquids at their boiling-points was published by Schiff[3] in 1884. He recognized that two liquids are really comparable only at their critical temperatures, but critical temperatures evidently could not be used to study capillarity, since this disappears at such temperatures.

A study of the molecular volumes of liquids at their boiling-points has shown that this temperature represents an analogous condition, since a constant difference in composition corresponds very nearly to a constant difference in molecular volume. Says Schiff,[1] "This consideration has led me to choose the boiling-point as the temperature for comparison, and to compare the capillarity constants determined at this temperature."

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[1] *Compt. rend.* **50**, 52; **51**, 97.

[2] *Pogg. Ann.* **121**, 44 (1864).

[3] *Lieb. Ann.* **223**, 47 (1884). An extensive bibliography is appended.

He first determined whether there is any relation between the molecular weights of substances and their capillary constants, by comparing the constants of substances having the same, or nearly the same, molecular weights and different constitution.

		Mol. Wt.	Capillarity Constant
Allyl alcohol,	C_3H_6O	57.87	5.006
Acetone,	C_3H_6O	57.87	5.189

It was found, in general, that for substances having nearly the same molecular weight, the constant was very nearly the same.

Those compounds of the fatty series, having the higher boiling-point, have the larger constant.

Among the aromatic compounds, that with the higher boiling-point has the smaller constant. With respect to their influence on capillarity, the elements bear to each other the following relations: —

$$C = 2\,H; \quad O = 3\,H; \quad Cl = 7\,H.$$

From these and similar data it was shown to be possible to calculate the capillarity constants of liquids from the chemical formulas.

Schiff's later work embraced a large number of substances, and he also studied the effect of temperature on surface-tension. His later work confirmed, in the main, the conclusions from his earlier investigations, but some exceptions were discovered.

A carbon atom is not always equivalent to two hydrogen atoms in its influence on surface-tension, but in some cases, as with the fatty acids, may be equivalent to three hydrogen atoms. A chlorine atom is generally equivalent to seven hydrogen atoms, but in some cases is equivalent to only six. A bromine atom is equivalent sometimes to thirteen, and sometimes to eleven, hydrogen atoms; iodine to nineteen hydrogen; nitrogen to two and to three hydrogen; and so on.

From the above it will be seen that capillarity is considerably affected by constitution, under some conditions.

Molecular Weights of Pure Liquids determined by Means of their Surface-tension. — The determination of the molecular weight of a pure homogeneous liquid is to be sharply distinguished from the determination of the molecular weight of one substance dissolved in another. As we shall see, we have excellent methods for solving the latter problem, but only one partially satisfactory method for the former. The work of the Hungarian physicist Eötvös[1] showed that the rate of change in surface-energy with the temperature is a constant. If γ is the surface-tension, s the surface, and t the temperature measured from the critical temperature as zero, we have —

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[1] *Lieb. Ann.* **223**, 53 (1884).

$$\frac{d\gamma s}{dt} = c.$$

That the formula might be applied to different liquids, s is taken as the molecular surface. If we represent the molecular volume by Mv, and regard this as a cube, any face of the cube will be $(Mv)^{\frac{2}{3}} = s$. The formula of Eötvös then becomes —

$$\gamma (Mv)^{\frac{2}{3}} = ct,$$

where t is the temperature of the experiment, calculated from the critical temperature downward.

Ramsay and Shields[2] tested the above formula experimentally, using a number of liquids whose molecular volumes were known; such as ether, methyl formate, ethyl acetate, carbon tetrachloride, benzene, chloroform, methyl alcohol, ethyl alcohol, and acetic acid. They must first determine the value of γ for each of the liquids. The surface-tension γ is calculated from the equation $\gamma = \frac{1}{2}\, rhg\, (\rho - \sigma)$, where r is the radius of the capillary tube, h the height to which the liquid rises in the tube, g the acceleration of gravity, ρ the density of the liquid at the temperature of the experiment, and σ the density of the vapor of the liquid. The value of h must be determined for each liquid over a considerable range of temperature. The apparatus finally used by Ramsay and Shields to measure the height to which the liquid rises in a capillary tube is shown in Fig. 13.

A glass tube A is fused at its two ends to two smaller glass tubes, B and C, and the latter is left open. D is a closed cylinder made of thin glass, containing a spiral of iron wire. It is fastened to a glass rod, and this in turn to the capillary FG. There is a small opening in the capillary at F. The capillary tube and the liquid to be investigated are introduced through C, and this is then drawn out as shown in the figure. The tube is then connected with a pump, and the liquid boiled until all the air has been removed. When the tube contains only the vapor of the substance, it is closed by fusion. The whole apparatus above the tube D is surrounded by a vapor-jacket, through which liquid or vapor of the desired temperature can circulate to keep the temperature of the inner vessel constant, and to bring it to the desired temperature. A magnet H, H is used to raise or lower the capillary so that the surface of the liquid inside the tube shall be only a few millimetres below the open end. The surface of the liquid is thus always brought to the same point in the capillary G, and the diameter of the tube at this point determined once for all. The height of the liquid column in the capillary is read by means of a telescope, at a definite temperature; the temperature varied as desired, and new readings made at given intervals.

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[1] *Wied. Ann.* **27**, 448 (1886).

[2] *Ztschr. phys. Chem.* **12**, 433 (1893).

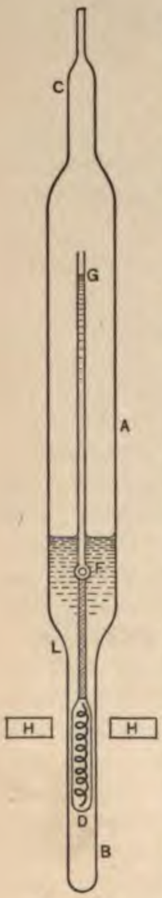

Fig. 13.

The results obtained by Ramsay and Shields showed that the formula of Eötvös does not hold at different temperatures, but for ether, methyl formate, ethyl acetate, carbon tetrachloride, benzene, and chlorbenzene, the following equation obtains: —

$$\gamma\,(Mv)^{\frac{2}{3}} = c\,(t - d).$$

d is small, being on the average about 5°. The equation holds for these substances to within a few degrees of the critical temperature. The average value of the constant for these substances is 2.12, varying between 2.04 and 2.22.

Methyl alcohol, ethyl alcohol, and acetic acid present exceptions. The value of c is not a constant, but varies with the temperature; therefore $\gamma\,(Mv)^{\frac{2}{3}}$ does not vary proportional to the temperature. That this may be true, M must vary with the temperature; or, in a word, the molecules of these substances are more complex at low temperatures than would correspond to the simplest formula, and these more complex molecules break down as the temperature rises. The substances which give the normal constant value of $c = 2.121$ are assumed to have the same molecular weight in the liquid as in the gaseous condition, since as the temperature approaches the critical temperature there is no change in the value of the constant. This, in most cases, is the simplest molecular weight possible for the substance. Liquids which do not give a constant value of c with change in temperature are known as "associated." The degree of association, or the association factor x, is obtained by dividing the value 2.121 by the value of the differential c, for the associated liquid at the temperature in question, thus: —

$$x^{\frac{2}{3}} = \frac{2.121}{c}, \text{ or } x = \left(\frac{2.121}{c}\right)^{\frac{3}{2}}.$$

The method of obtaining c for a non-associated liquid, and for an associated liquid, and x, the association factor, will be made clearer by an example taken from the work of Ramsay and Shields.[1]

Take first a non-associated liquid — carbon bisulphide: —

γ at 19°.4 = 33.58 $\quad\quad$ $\gamma(Mv)^{\frac{2}{3}}$ at 19°.4 = 515.4
γ at 46°.1 = 29.41 $\quad\quad$ $\gamma(Mv)^{\frac{2}{3}}$ at 46°.1 = 461.4

The value of the differential between these two temperatures is —

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{515.4 - 461.4}{46.1 - 19.4} = 2.022.$$

Since this value differs so slightly from the mean value 2.121 for non-associated liquids, we conclude that carbon bisulphide belongs to this class.

Let us take as an example of an associated liquid formic acid: —

γ at 16°.8 = 37.47 $\quad\quad$ $\gamma(Mv)^{\frac{2}{3}}$ at 16°.8 = 424.4
γ at 46°.4 = 34.42 $\quad\quad$ $\gamma(Mv)^{\frac{2}{3}}$ at 46°.4 = 397.7
γ at 79°.8 = 30.80 $\quad\quad$ $\gamma(Mv)^{\frac{2}{3}}$ at 79°.8 = 364.6

Between the first two temperatures we have —

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{424.4 - 397.7}{46.4 - 16.8} = 0.902.$$

Between the second and third —

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{397.7 - 364.6}{79.8 - 46.4} = 0.991.$$

The value of c differs greatly from the normal value 2.12 for non-associated substances, and, therefore, the molecules of formic acid are associated into complexes.

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[1] *Ztschr. phys. Chem.* **12**, 462 (1893).

It still remains to calculate the value of the association factor x. For the range between 16°.8 and 46°.4, we have —

$$x = \left(\frac{2.121}{0.902}\right)^{\frac{3}{2}} = 3.61.$$

For temperatures between 46°.4 and 79°.8 —

$$x = \left(\frac{2.121}{0.991}\right)^{\frac{3}{2}} = 3.13.$$

The molecular weight of the substance in the liquid condition is obtained by multiplying the association factor by the simplest molecular weight of the substance. The molecular weight of formic acid between the lower temperatures is $3.61 \times 46 = 166$; between the higher temperatures, $3.13 \times 46 = 144$.

As the temperature increases the molecular weight decreases, showing that at the higher temperature the complex molecules undergo some dissociation into simpler molecules. Ramsay and Shields[1] determined the surface-tension of a large number of liquids at different temperatures, and calculated the value of the differential between the temperatures used. He found that many liquids gave the normal value 2.12, while many others gave values which were much smaller. Among the former or non-associated liquids are phosphorus trichloride, ethyl iodide, ether, chloral, ethyl formate, ethyl acetate, benzene, chlorbenzene, nitrobenzene, aniline, pyridine, etc. The associated liquids include the alcohols, the fatty acids, acetone, phenol, water, and the like.

The molecular weights of the associated liquids show that the molecules of such liquids do not, in general, contain a large number of the simplest molecules. Liquid phosphorus, however, seems to contain four atoms of phosphorus in the molecule (P_4), and water has the most highly associated molecule of any compound studied. The results of measurements of surface-tension show that the molecular weight of water at 0° corresponds to the formula $(H_2O)_4$. Water thus stands at the extreme with respect to its molecular complexity in the liquid condition. We shall see later that most of the properties of water are exceptional. They are usually exceptionally large or small, placing water at one extreme or the other of the substances with which it can be compared.

As a further test of the accuracy of the formula $\gamma(Mv)^{\frac{2}{3}} = c(t - d)$, and the constancy of c for normal liquids, a number of esters were carefully studied; their surface-tensions being measured from 10° to to 240°.[1] The value of c for eight esters varied from 2.04 to 2.25. That the value of c is approximately constant for normal liquids seems thus to be established beyond question.

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[1] *Ztschr. phys. Chem.* **12**, 464 (1893). *Journ. Chem. Soc.* **63**, 1089 (1893).

In this method of determining the molecular weights of pure liquids, it was assumed that the molecular weight of normal liquids is the same as in the gaseous state. Although this is an assumption, it is made very probable by the fact that if there is an association in normal liquids, the same number of gaseous molecules must be associated in the liquid molecules of all such substances, since c is a constant for all normal liquids. This is extremely improbable. The assumption that there is no association in normal liquids is further very much strengthened by the fact, that as the temperature rises and approaches the critical temperature there is no sign of any dissociation of the molecules of such liquids into simpler molecules — the value of c remaining constant close up to the critical temperature. This is scarcely possible if the molecules of these substances consist of complexes, since it is almost certain that such complexes would begin to break down long before the critical temperature was reached.

The method employed by Ramsay and Shields to calculate the value of the association factor x is, however, still open to some doubt. Somewhat later Ramsay[2] proposed a better method of calculating the value of this quantity, but even this does not seem to be entirely free from objection. The surface-tension method enables us, then, to distinguish between liquids which are not associated and those which are; it probably makes it possible to determine very roughly the degree of association, or the number of the simplest molecules combined to form the liquid molecule.

DIELECTRIC CONSTANTS OF LIQUIDS

The Dielectric Constants of Some of the More Common Solvents. — The dielectric constant, or specific inductive capacity of liquids has recently acquired a very special interest from the physical chemical standpoint, due to a relation which is supposed to exist between this property and the power of liquids to break down molecules into ions. This relation will be taken up later, when the dissociating power of different liquids is under consideration.

The meaning of the term "dielectric constant of a medium" is best illustrated, perhaps, as follows: When two charges of electricity are placed at a certain distance apart and separated by a dielectric, the force with which they act upon one another is proportional to the product of the two quantities, and inversely proportional to the square of the distance between them. But it was shown by Faraday that the nature of the non-conducting medium between the two charges must be taken into account. A factor must be introduced for the nature of this medium. This factor, which is a constant for any given medium, was termed by him the specific inductive capacity of the medium, and has since come to be known as the dielectric constant of the medium.

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[1] *Ztschr. phys. Chem.* **15**, 98 (1894). *Proc. Roy. Soc.* **56**, 162 (1894).

[2] *Ibid.* **15**, 111 (1894).

A number of methods have been devised for determining dielectric constants. We should mention especially those of Thwing,[1] Nernst,[2] and Drude.[3]

The dielectric constants of some of the more common solvents at 18° are given in the following table:—

	DIELECTRIC CONSTANT
Hydrogen dioxide	92.8 ?
Water	77.0
Formic acid	63.0
Nitrobenzene	36.0
Methyl alcohol	33.7
Ethyl alcohol	25.9
Propyl alcohol	22.0
Ammonia, liquid	22.0
Amyl alcohol	16.0
Ethylene chloride	11.0
Aniline	7.3
Chloroform	5.0
Ether	4.4
Carbon bisulphide	2.6
Benzene	2.3

It was thought for a long time that water has the highest dielectric constant of any known solvent. When solutions of salts in liquid ammonia were shown to have high conductivity, it was supposed that the dielectric constant of liquid ammonia would be very high. The work of Goodwin and Thompson[4] showed, however, that such was not the case, the constant for liquid ammonia being only about 22. The effort to find a solvent with a higher dielectric constant than water was continued, and has apparently been crowned with success. Calvert[1] has shown, from a study of the dielectric constant of an aqueous solution of hydrogen dioxide, that it is probably higher than that of water, having the value given in the table. There is thus one liquid known which probably surpasses water with respect to this property. This, however, is not proved as yet, and even if it is true is not very surprising, since hydrogen dioxide is so closely allied to water in composition, being in a certain sense water intensified.

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[1] *Ztschr. phys. Chem.* **14**, 286 (1894).

[2] *Ibid.* **14**, 622 (1894).

[3] *Ibid.* **23**, 267 (1897).

[4] *Phys. Rev.* **8**, 38 (1899).

A survey of this chapter will show that there is a close relation between many of the physical properties of liquids and their composition and constitution. Many of these relations are thus far purely empirical, their meaning and significance being entirely unknown. Yet, in most cases, such relations have been clearly established beyond question, by very elaborate and careful investigations. While at present we fail to see the real significance of most of these relations, we cannot but recognize their great importance. The introduction of an atom or a group of atoms, producing a constant effect on so many physical properties, or the constant influence of a double or triple bond, are facts which must lie very close to the ultimate composition and constitution of matter. We feel, instinctively, that there is some generalization of the very deepest significance foreshadowed, as it were, by facts such as those considered in this chapter; and instead of these empirical generalizations being neglected, they should stimulate to renewed effort to discover what they really mean. While it is impossible at present to predict from what quarter light will be thrown on such facts, it is not improbable that the study of the thermal phenomena manifested by liquids, such as specific heat, absolute boiling-temperature, etc., may prove helpful in the direction indicated. There is no chapter in the older or the newer physical chemistry where a wide-reaching generalization is more needed, and none in which a comprehensive generalization would contribute more toward placing chemistry upon the basis of an exact science.

[1] *Ann. der Phys.* 1, 483 (1900).

CHAPTER IV

SOLIDS

General Properties of Solids. — The third state of aggregation of matter is known as the solid state. We have seen that when any gas is cooled below a certain point it passes over into the liquid state. When any liquid is cooled sufficiently it passes over into a solid. It is thus possible to pass from the gaseous or liquid state to the solid. The reverse transformation is also possible, — a solid can be converted into a liquid by heat, and, as we have seen, a liquid can be transformed into a gas. Every elementary form of matter may take any of the three states of aggregation — gas, liquid, or solid; the state in which it exists at any given time is determined by the temperature and pressure to which it is subjected. By varying these sufficiently and in the right direction, it can be made to take either of the other forms.

We have already studied the general characteristics of the gaseous and liquid states; we shall now turn to the general properties of solids. The most striking difference between solids, and liquids and gases is that the first has a definite form and occupies a definite space. In respect to these properties, solids differ fundamentally from the other states. Another striking difference which really lies at the foundation of those just referred to, is the relative rigidity of the parts in a solid. The particles are firmly fixed, and move over one another only with the greatest difficulty, enormous pressures being required to change the form of solids. As it is said, the resistance to movement or the inner friction of solids is very great. With liquids there is some inner friction, but relatively little, while with gases the resistance to the movement of the parts is relatively quite small.

Solids behave very differently from gases with respect to their power to resist pressure. The volume of gases is changed by pressure, approximately according to the law of Boyle — volume varies inversely as pressure. The volume of solids is changed but little, even when the pressure is very great. In this respect the difference between solids and liquids is much less than between solids and gases.

Liquids are compressed but little by great pressure, but the change in volume is greater than with solids.

The density of solids is much greater than that of gases, and, in general, greater than that of liquids. This is just what we would expect, since the solid state represents matter in the most condensed form. It is true that some liquids are heavier than some solids, but the above statement is generally true.

The change in the volume of solids produced by heat is much less than for gases. The temperature coefficient of the latter is, as is well known, $\frac{1}{273}$, while the volume of solids changes only a small fraction of this amount for a change of one degree in temperature.

The solid state not only represents matter in its most concentrated form, but, as we have seen, in its most resistant state; resistant not only to physical agents, but also to chemical. While a substance remains a solid it is much less active chemically than when in either of the other states of aggregation. In many cases a solid will not react at all with another substance, but when it is melted reacts readily. The result is, we know much less of the chemistry of solids than of liquids and gases. The same holds true with respect to our physical chemical knowledge of solids. Partly on account of the relative inertness of solids, and partly because of a lack of efficient methods with which to study them, we know relatively little of matter in the solid state from the physical chemical standpoint. Much that is included in some works on physical chemistry with respect to solids, seems to belong either to pure physics or to the science of crystallography and mineralogy. The subject of solids can be dealt with very briefly by the physical chemist, and, consequently, this chapter is quite short.

CRYSTALS

Crystal Systems. — Most of the solid substances with which we are familiar tend to take certain definite geometrical forms, which are more or less characteristic of the substance. This is true whether the solid is formed from a homogeneous liquid or from solution. In the latter case, however, there is generally better opportunity for the particles to arrange themselves according to their attractive forces, and, consequently, well-defined crystals are more frequently formed from solution than from a pure liquid. In a crystal the particles are arranged in a perfectly orderly manner, and fulfil the condition that the arrangement about any one point is the same as about any other point.

Crystals fall into a number of groups or systems, with respect to the nature of their crystallographic forms. Indeed, six such crystallographic systems are recognized.

I. Some crystal forms are built up upon three axes which are all of the same length, and are all at right angles to one another. This system, known as the **regular** or **isotropic** system, is distinguished from the remaining systems in that all the properties of the crystals are the same in every direction. This system includes such well-known forms as the octohedron, cube, dodecahedron, etc. The regular system is distinguished from all the other crystallographic systems, in that it has the largest number of planes of symmetry.

II. The **tetragonal** system comprises all of those forms which are built upon two axes of the same length and the third axis of a different length from the other two; all the angles between the axes being right angles. In such crystals the axis which is longer or shorter than the other two is placed vertically, and the two axes of equal length are placed, therefore, in the horizontal plane. The symmetry here is evidently of a lower order than in the regular system.

III. A third crystallographic system is conceived as built upon three axes symmetrically arranged in a horizontal plane, all of equal length, and making right angles with a vertical axis which is of different length. It is evident that this system, called the **hexagonal**, is closely related to the tetragonal from a geometrical standpoint, and we shall see that crystals in the two systems resemble one another closely with respect to their physical properties.

IV. The **orthorhombic** system has three axes all of unequal length, but all making right angles with one another. It is evident that the symmetry of the geometrical forms built upon such axes is lower than in any other system thus far considered.

V. The above four systems have all the axes making right angles with one another, except the hexagonal system which has three lateral axes, and these make angles of sixty degrees with one another. There are crystallographic systems in which the axes do not make right angles with each other. The first of these — the **monoclinic** — has all three axes of unequal length, and one of them not making a right angle with the other two. The presence of the oblique angle has evidently reduced the degree of symmetry very nearly to its limit. Indeed, in the monoclinic system there is only one plane of symmetry remaining — the plane of the oblique and vertical axis. There is only one more step possible in decreasing the symmetry of a system, and that is realized in the sixth and last crystallographic system.

VI. In the **triclinic** or **asymmetric** system the three axes are all of unequal lengths, and are all inclined to one another. There is no right angle in this system, and, therefore, no plane of symmetry. The triclinic system stands, then, at one extreme, in which all symmetry has been lost, while the regular system represents the highest degree of symmetry.

Holohedrism. Hemihedrism. Tetartohedrism. — A given crystal form may occur with all the planes present as an octahedron, a prism, a pyramid, etc. When all the planes belonging to a given form occur, we have a complete or holohedral crystal.

It frequently happens, however, that only half the planes belonging to a given form occur. These are then extended until they meet and give a figure which is quite different from the holohedral form from which they are derived. Thus, the hemihedral form of the octahedron is the tetrahedron; of the hexagonal prism the rhombohedron, etc.

In a similar manner only one-fourth of the planes of the holohedral form may occur. In this way tetartohedral forms are produced, and examples of tetartohedrism are not wanting.

Importance of Crystallography for Chemistry and Physical Chemistry. — The subject of crystallography has an important chemical and physical chemical bearing. A given substance not only crystallizes in certain characteristic forms, but the angles between the planes are constant for the same substance. This fundamental law of crystallography is known as the law of Steno. The crystal form and size of the angles thus become important constants for any given substance, and are of the very greatest importance in identifying chemical compounds. Further, since different substances usually have different forms, and always different angles if they have the same form, we utilize the form of crystals to determine the purity of the substance with which we are dealing. If from a solution or molten mass more than one form of crystals separates, we are generally justified in concluding that we are dealing with a mixture. In some cases, however, the same substance crystallizes in more than one form, so that the above conclusion is not always valid, but such cases are relatively not common. On the other hand, two substances may crystallize in apparently the same form; *e.g.* calcium carbonate and magnesium carbonate as dolomite. In such cases, while the form appears to be the same the angles made by the faces depend upon the composition. The angles on a pure calcite crystal differ from those on dolomite, and, indeed, the angle can be used to determine the amount of magnesium carbonate present in the dolomite.

We thus see from the above that while crystal form alone is not always an absolute guarantee of the purity of a substance, it is of very great aid to the chemist in determining whether he is working with a chemical individual or with a mixture. All that has been said above in reference to the application of crystallography to chemistry, applies with equal force to physical chemistry. In all physical chemical work the question of the purity of the substance is fundamental, and the crystallographic method is, as we have seen, of great assistance in this connection. The application of crystal form to a physical chemical problem of the very highest importance has already been studied. It will be remembered that Pasteur separated dextro and lævo tartaric acids by means of certain hemihedral faces, which occurred on the ammonium sodium salts of these acids — one hemihedral form occurring on some crystals, the other form on other crystals. And this was the beginning of what has been developed into an entirely new branch of science; viz. stereochemistry.

However, in addition to all this, the form of crystals has still another interest for the physical chemist. When the physical properties of crystals were studied, it was found that there are certain very close connections between these properties and the geometrical form of the crystal. To some of these relations we will now turn.

PROPERTIES OF CRYSTALS. RELATIONS BETWEEN FORM AND PROPERTIES

Optical Properties. — The six crystal systems which we have just considered fall into three classes with respect to their action on light. The first class includes the regular system. The substances which crystallize in this system have only the power to refract light, but no power to doubly refract it. This holds for every direction in which the light is passed through the crystal. A large number of apparent exceptions to this generalization have been observed. Many substances which crystallize in the regular system have been found to show double polarization. This phenomenon has been satisfactorily explained as due to a lamellar arrangement within the crystal, or to a certain stress or strain in the crystal produced during its growth, or to a combination of individuals which form an apparently isometric crystal. Since so many crystals in the regular system show no double refraction, it is evidently not a characteristic of the system, but an accidental state which obtains under certain conditions of growth.

The second class includes the tetragonal and hexagonal systems. These have one optic axis, and hence are termed uniaxial. If a ray of light is passed through the crystal along this axis, which is parallel to the vertical axis of the crystal, *i.e.* the axis which differs in length from the other two, there is no double refraction. The three remaining crystallographic systems fall into the third class. There is no direction through crystals in these systems in which light passes as through an isotropic substance. They have no isotropic axis. There are, however, two directions through such crystals in which the two rays into which light is broken travel with the same velocity. These are known as the optical axes, and hence such crystals are termed biaxial.

The relations between crystallographic form and optical properties become perfectly clear when we regard light as a vibratory motion of the ether. We must regard the crystallographic axes as expressing the relative densities of the ether in the different directions through the crystal. Thus, when all the axes are of the same length, the density of the ether is the same in all directions through the crystal. When the axes are of different lengths, the ether is unequally dense in the different directions. Applying these conceptions to the different crystallographic systems, we are impressed by the beautiful agreement between theory and fact. In the *regular or isotropic system* the axes are all of equal length; therefore, the ether is equally dense in all directions through such crystals. Light would then move in all directions through such crystals with equal velocity, and, consequently, there could be no double refraction.

In the *uniaxial systems* (tetragonal and hexagonal) the ether is equally dense in the directions of the axes of equal length, but more or less dense in the direction of the axis of unequal length. If light is passed through such crystals in any direction except parallel to the axis of unequal length, it will encounter ether of unequal densities in the different directions. Consequently, the ray of light will be broken up into two rays, or, as we say, will be doubly refracted. If the ray passes through the crystal parallel to the axis of unequal density, it will encounter ether of equal density in all directions, since the axes normal to this axis are of equal length. The ray will not be broken up into two when it moves in this direction, or, as we say, is not doubly refracted.

When we come to the *biaxial systems*, the problem is much more complicated. The three axes are all of unequal length, and, therefore, the densities of the ether are different in the directions of the three axes. A ray of light passed through the crystal along any crystallographic axis will necessarily be broken up into two. There are, however, two directions through such crystals, in the plane of greatest and least density, along which the two beams of light move with equal velocity. These two optic axes are placed symmetrically with respect to the directions of least and greatest density. These directions may, or may not, coincide with the crystallographic axes, depending upon the system. In the orthorhombic system these directions coincide with the crystallographic axes. In the monoclinic system only one of these directions is coincident with the crystallographic axes, — the one perpendicular to the plane of symmetry, — while in the triclinic system neither of these directions is coincident with the crystallographic axes.

The phenomenon of polarization of light by crystals is a necessary consequence of the difference in density of the ether in different directions through the crystal. If the ray encounters ether of different densities, it is broken up into two rays, whose vibrations are in planes at right angles to one another. Light whose vibrations are reduced to a single plane is said to be polarized. These two polarized rays move through the crystal with different velocities — the velocity being conditioned by the density of the ether. Knowing the relation between crystallographic form and density of the ether in the crystal, we are able to predict with certainty in just what cases light will be polarized by passing it through any given crystal.

A close relationship between the geometrical forms of crystals and their optical properties is thus evident. Indeed, the form is an index to the condition of the ether in the crystal — a geometrical expression of the relative densities of the ether in different directions through the crystal.

Thermal Properties of Crystals. — The thermal properties of crystals, which will be considered here, are the expansion of crystals by heat and the thermal conductivity of crystals. Only crystals in the regular system expand equally in all directions with rise in temperature. Crystals in all of the other systems expand differently in different directions. Fizeau[1] has shown that crystals in the tetragonal and hexagonal systems expand equally in two directions, and differently in the third direction. This corresponds perfectly with the geometrical form and optical properties of such crystals. The effect of temperature on crystals in the different systems can best be illustrated thus: If a sphere is cut from a crystal in the regular system at any given temperature, it will remain a sphere at all temperatures. If a sphere is cut from a crystal in the tetragonal or hexagonal systems, at any temperature, it will not be a sphere at any other temperature, since the expansion along one axis is different from that along the other two — it will become an ellipsoid of revolution. If the crystal is orthorhombic, monoclinic, or triclinic, it will expand differently in all three directions, and, consequently, the sphere will become a triaxial ellipsoid.

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[1] *Compt. rend.* **66**, 1005, 1072.

The *conductivity of heat* by crystals obeys the same laws as the optical conductivity. The thermal conductivity was studied by boring small holes in plates of crystals, inserting a warm wire into the hole, and observing the melting of a layer of wax with which the plate was covered. In crystals of the regular system the figure of the melted wax was always a circle; in uniaxial crystals a circle or ellipse, depending upon whether the plate was cut perpendicular to the optic axis, or parallel to it. In biaxial crystals the figure of the melted wax was always an ellipse.[1] These facts will be seen to be perfectly analogous to the action of crystals on light, and also to their thermal expansion.

Electrical Conductivity. — Our knowledge of the electrical conductivity of crystals we owe chiefly to G. Wiedemann.[2] Plates of crystals were covered with some non-conducting powder, such as lycopodium or minium. Above these an isolated fine point was suspended and charged positively by means of a Leyden jar. The powder was repulsed from the charged point, in the form of a circle with isometric crystals, but approximately in the form of an ellipse with other crystals. The powder renders visible the distribution of electricity over the surface of the plate of crystal, and from the figure we can see the relative electrical conductivities in different directions.

Wiedemann found that electricity is conducted through crystals most rapidly in the directions in which light moves most rapidly. The results show that the electrical properties of crystals agree also with their thermal properties.

We thus have a close connection between the optical, thermal, and electrical properties of crystals, and what is of even greater interest, a close connection between these properties and the geometrical forms of the crystals. Other properties of crystals could be taken up if space permitted, such as the figures produced by etching the crystals, the hardness and elasticity of crystals, etc.; but the more important properties considered above show beyond question that the form which matter takes in the crystal is either conditioned by, or more probably conditions, the state of strain or stress to which the ether is subjected. There is thus a striking agreement between the form of the crystal and its properties, which depend upon the condition of the ether in the crystal.

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[1] Sénarmont: *Ann. Chim. Phys.* [3], **21**, 457 (1847); **22**, 179 (1848). *Pogg. Ann.* **73**, 191 (1848); **74**, 190 (1849); **75**, 50 (1849). Lang: *Pogg. Ann.* **135**, 29 (1868).

[2] *Pogg. Ann.* **76**, 404 (1849).

CRYSTALLOGRAPHIC FORM AND CHEMICAL COMPOSITION

Polymorphism. — The conclusion might be drawn from what has been stated, that a definite chemical substance always crystallizes in the same form, which is characteristic of the substance. While this is generally true, it is by no means always so. The same element or compound may crystallize in more than one form, and the forms may even have different degrees of symmetry. When the same substance crystallizes in two forms, it is called *diamorphous;* when in more than two, *polymorphous.* Sulphur is a good example of an element which crystallizes not only in more than one form, but also with different symmetry. As found in nature it is orthorhombic; but if molten sulphur is allowed to cool under certain conditions, it crystallizes in the monoclinic system. Calcium carbonate is an example of a compound crystallizing in more than one system. As calcite it crystallizes in the hexagonal system, while as aragonite it belongs to the orthorhombic system. Other substances are known which crystallize in more than two forms, and so on.

There are a number of conditions which determine the form which a given substance will take. Of these the most important is temperature. This is shown very well in the case of sulphur. At the higher temperature the monoclinic form seems to be the most stable, while at lower temperatures the orthorhombic represents the more stable condition. The monoclinic form passes over readily into the orthorhombic at lower temperatures.

In connection with the effect of temperature on molecular structure, reference should be made to the recent work of Cohen[1] on tin. He has found that ordinary white tin is stable only above 20°. Below this temperature it passes over slowly into a gray crystalline modification, which has very different properties from the ordinary white tin. The gray modification when heated above 20° passes rapidly back into the white again. While the exact crystallographic change which takes place has not yet been worked out, it is quite certain that the transformations in the case of tin are strictly analogous to those which take place with sulphur.

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[1] *Ztschr. phys. Chem.* **30**, 601 (1899); **33**, 57 (1900); **35**, 588 (1900).

Conditions other than temperature also affect the crystal form. The presence of even a small amount of a foreign substance may condition the form in which another substance will crystallize. Take the case of calcium carbonate, which can crystallize in either the hexagonal or orthorhombic system. If a substance is present which crystallizes in the hexagonal system, the carbonate of calcium will be much more liable to form hexagonal crystals; but if some orthorhombic substance is present, the carbonate will more probably form orthorhombic crystals. The influence which one substance may have on the form which another will take, may even be so great as to force it to take a form in which it would never crystallize if left to its own forces.

The examples of polymorphism given above all represent the condition where each of the forms can be transformed into the other by heat or some other agent. There are, however, cases known where a substance crystallizes in two forms, which have thus far not been transformed into one another. Thus, diamond and graphite have not been mutually transformed into one another, although the latter has been obtained from the former. That there is really any inherent difference between this case and those above considered, where such reciprocal transformations have been effected, no one can believe. The two or more forms in which the same kind of matter occurs, represent, as we shall see, but different conditions of energy. The one form contains more energy stored up within itself than the other, and hence the difference in properties, including the difference in crystal form. The one form is the more stable under certain conditions of temperature, etc., while another modification is the more stable under other conditions. The meaning of this will be clearer when we come to see the significance of energy relations as conditioning the properties of substances in general.

Isomorphism. — It is evident from the last paragraph that the same substance may crystallize in more than one form. This raises the question as to whether different substances ever crystallize in the same form. This question was answered once for all by Mitscherlich. In an investigation[1] carried on in part in the laboratory of Berzelius, he showed that a number of different substances may crystallize in the same form, and then completed an elaborate investigation in the same laboratory on the arseniates and phosphates. He found that these salts, although quite different chemically, crystallize in forms which are so nearly identical that it was impossible to detect with certainty any appreciable differences. As the result of this work Mitscherlich was led to the following generalization:[1] —

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[1] *Ann. Chim. Phys.* [2], **14**, 172 (1820).

"*The same number of atoms combined in the same manner produce the same crystalline form; and the same crystalline form is independent of the chemical nature of the atoms, and is determined only by the number and relative position of the atoms.*"[1]

This conclusion, as is well known, went too far beyond the facts, yet it has considerable historical interest in connection with the determination of atomic weights, as we have seen. It is now well known that there are substances with the same crystalline form, whose molecules contain very different numbers of atoms. The work of Mitscherlich established the fact of isomorphism, and showed that a crystal would grow as well in a solution of an isomorphous substance as in its own. He showed that a number of single sulphates may grow into the same crystal, also that an alum crystal may contain a number of alums.

In the light of polymorphism and isomorphism, one would naturally ask, can crystal form be used at all as a characteristic of chemical composition? The answer is, it can. Most substances crystallize under ordinary conditions in characteristic forms, and crystal form has been of the very greatest service in identifying and testing the purity of chemical substances.

MELTING-POINTS OF SOLIDS

Method of Determining the Melting-point. — The method of determining the melting-point of a solid, which is generally employed, is very rough. The solid is placed in a fine glass tube closed at the bottom, and attached to a thermometer. The whole is then immersed in sulphuric acid in a small glass bulb, and the acid warmed to the melting-point of the solid. It is evident that such a method can give only approximate results, however slowly the sulphuric acid is heated. There is nothing to protect the thermometer from the effect of radiation, and the warm bulb is constantly radiating heat outward on to the colder objects around it. In order that any measurement of temperature should be accurate, it is necessary that the bulb of the thermometer should be surrounded by a metallic screen, as nearly as possible at its own temperature. In making an accurate melting-point determination, the bulb of the thermometer should be surrounded by a screen of platinum foil, which is also immersed in the same liquid as the thermometer in order that it may be heated to the same temperature. Since this precaution has been for the most part disregarded, the melting-point determinations, especially of organic compounds, may contain some considerable error.

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[1] *Ann. Chim. Phys.* [2], **19**, 419 (1821).

The above method is employed when only a small amount of substance is at disposal. If a larger amount is available, the whole mass may be heated above its melting-point and converted into liquid. The liquid can then be carefully cooled down to its freezing-point, which is the same as the melting-point of the solid. In this case the liquid is almost certain to suffer undercooling, *i.e.* to cool below its freezing-point before solidification begins. This will often take place even when the entire mass of the liquid is vigorously stirred. Undercooling can be prevented by adding a small fragment of the solid substance. When the liquid has cooled a trifle below its freezing-point, it is only necessary to add a small particle of the solid, when all undercooling will be removed by the separation of more of the solid substance, which will warm the remainder of the liquid up to its true freezing-point. It is only necessary to read the temperature of the liquid containing some of the solid phase of the substance, on an accurate thermometer, at standard pressure, and we have the true melting-point of the substance.

An almost infinitesimal quantity of the solid phase is sufficient to cause an undercooled liquid to freeze. In this connection reference only can be made to a recent paper by Ostwald,[1] which records some very surprising results bearing upon this point.

Relations between the Melting-points of Substances. — Certain regularities between the melting-points of the elements have already been pointed out. We will consider here some relations which have been discovered between the melting-points of compounds. The bromine compounds[2] melt higher than the corresponding chlorine compounds, and the nitro compounds higher than the bromine compounds. Of the disubstitution products of benzene the para compounds, in general, melt higher than the ortho or meta. A relation which is far more interesting than the above has been pointed out by Baeyer.[3] In studying the oxalic acid series Baeyer noticed that *those compounds which have an even number of carbon atoms melt higher than those with an odd number.*

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[1] *Ztschr. phys. Chem.* **22**, 289 (1897).

[2] Peterson, *Ber. d. chem. Gesell.* **7**, 58 (1874).

[3] *Ibid.* **10**, 1286 (1877).

	Melting-point
Succinic acid, $C_4H_6O_4$	180°
Pyrotartaric acid, $C_5H_8O_4$	97°
Adipic acid, $C_6H_{10}O_4$	148°
Pimelic acid, $C_7H_{12}O_4$	103°
Suberic acid, $C_8H_{14}O_4$	140°
Azelaic acid, $C_9H_{16}O_4$	106°
Sebasic acid, $C_{10}H_{18}O_4$	127°
Brassylic acid, $C_{11}H_{20}O_4$	108°

A similar regularity was observed with the normal members of the formic acid series: —

	Melting-point		Melting-point
Acetic acid, $C_2H_4O_2$	+ 17°	$C_8H_{16}O_2$	+ 16°
Propionic acid, $C_3H_6O_2$	lower than – 21°	$C_9H_{18}O_2$	+ 12°
Buturic acid, $C_4H_8O_2$	0°	$C_{10}H_{20}O_2$	+ 30°
Valeric acid, $C_5H_{10}O_2$	lower than – 16°	$C_{16}H_{32}O_2$	+ 62°
Caproic acid, $C_6H_{12}O_2$	– 2°	$C_{17}H_{34}O_2$	+ 59°.9
Œnanthylic acid, $C_7H_{14}O_2$	– 10°.5	$C_{18}H_{36}O_2$	69°.2

In both series, the members with an odd number of carbon atoms have lower melting-points than their two adjoining members with an even number of carbon atoms. The meaning of this regularity is entirely unknown.

Quite recently Bayley[1] has shown that the ratio between the melting-points and boiling-points of a number of hydrocarbons of the paraffine, ethylene, and acetylene hydrocarbons is nearly a constant. It may vary from 1.5 to 2 within a given series, but usually much less. The author attempts to connect the constitution of the compound with the value of this ratio.

Melting-point a Criterion of Purity. — Of all the methods available for identifying a substance and testing its purity, no one is so frequently made use of by the chemist as the melting-point method. The temperature at which a substance melts is a characteristic constant for the substance, and this is often used as one means of identifying it. Further, if the substance is pure it will melt sharply at one temperature. If the melting-point is not sharp, a part of the substance melting at one temperature and the remainder not until a higher temperature is reached, we must conclude that the compound is not pure, and that we are dealing with a mixture. The presence of a very small amount of a foreign substance affects the melting-point quite considerably, usually producing a lowering of this point, so that a sharp melting-point means a high degree of purity.

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[1] *Chem. News*, **81**, 1 (1900).

LATENT HEAT OF FUSION

Latent Heat, and Molecular Latent Heat of Fusion. — When a solid is heated up to a certain temperature it begins to melt. If more heat is added at this temperature, the solid continues to melt, but the temperature does not rise until all of the solid has passed over into the liquid condition. During the process of melting, a large amount of heat is consumed and disappears as such. This was early termed "latent heat," and the name still persists. The amount of heat required to melt one gram of a substance at a fixed temperature is termed the *latent heat of fusion* of the substance at the temperature in question. This quantity multiplied by the molecular weight of the substance gives the *molecular heat of fusion.* When the melted substance solidifies, exactly the same amount of heat is given out as was consumed in melting it.

The latent heat of fusion of a solid is perfectly analogous to the latent heat of vaporization of a liquid. It will be remembered that when a liquid is heated to the boiling-point, and more heat is added, the temperature does not rise, but the liquid passes over into vapor. The heat required to convert a liquid into vapor is usually very large; indeed, the latent heat of vaporization is much greater than the latent heat of fusion. The large amount of heat consumed in passing from the solid to the liquid state, and from the liquid to the gaseous condition, does internal work driving the molecules farther apart, and producing in general a molecular rearrangement.

Determination of Latent Heat of Fusion. — The method of measuring the latent heat of fusion consists not in measuring the amount of heat which must be added in order to fuse a given quantity of any substance, but in measuring the heat liberated by a given quantity of a molten substance at its melting-point when it solidifies. This heat of solidification is exactly equal to the latent heat of fusion.

The latent heat of fusion of liquids, like their latent heat of vaporization, is of importance in physical chemistry, as we shall see, because of certain theoretical relations which have been worked out between this quantity and the lowering of the freezing-point of a solvent by a dissolved substance. The latent heat of fusion of a few of the more common solvents is given in the following table: —

	Latent Heat of Fusion
Ice	79.7 cal.
Benzene	29.1 cal.
Nitrobenzene	22.3 cal.
Formic acid	58.4 cal.
Acetic acid	43.7 cal.

SPECIFIC HEAT OF SOLIDS

Law of Dulong and Petit. — Although a portion of the material belonging to this section has necessarily been anticipated in the discussion of methods for determining atomic weights, the subject will now be taken up a little more systematically. A relation between the specific heats of solid elementary substances and their atomic weights was discovered as early as 1819 by Dulong and Petit.[1] A few examples from their paper will make this relation clear: —

	Specific Heat	Atomic Weight	Product
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Copper	0.0949	3.957	0.3755
Iron	0.1100	3.392	0.3731
Sulphur	0.1880	2.011	0.3780

These atomic weights are referred to oxygen as unity. The value of the "product" must be multiplied by 16 to obtain the value assigned to it to-day. The product of the specific heat by the atomic weight is known as the atomic heat; and this is very nearly a constant for the different elements.

Work of Regnault. — The law of Dulong and Petit was thoroughly tested some twenty years later by Regnault,[2] who worked with a large number of elementary substances. He found that the law is in the main true, but the atomic heats are not the same for the different elements; they are only approximately a constant. The subsequent work of Regnault on the specific heats of the elements brought out a number of interesting facts. He showed that the atomic weights of a number of the elements must be only half[1] the values previously assigned to them, in order that the law of Dulong and Petit might apply to these substances. He, however, found certain elements to which the law of Dulong and Petit did not apply at all. The specific heat of different kinds of carbon[2] was determined, and found to vary greatly with the nature of the material. The lowest value, 0.146, was found with the diamond, and the highest, 0.260, with animal charcoal. Values ranging all the way between these two extremes were found with graphite, anthracite, coke, and wood charcoal. This was evidently at variance with the law under consideration, and especially so since the highest value found was far too low to accord with the law.

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[1] *Ann. Chim. Phys.* [2], **10**, 395 (1819).

[2] *Ibid.* [2], **73**, 5 (1840).

Regnault[3] discovered the same discrepancy in the cases of silicon and boron. Their specific heats were far too low to give the nearly constant value of the atomic heat, when it was multiplied by the atomic weight of the element.

Work of Kopp. — The work of Kopp,[4] published nearly twenty-five years later than that of Regnault, added greatly to our knowledge of the specific heat of solids. It is impossible to enter into the details of this tremendous piece of work; only a few of the conclusions reached can be pointed out. The law of Dulong and Petit was found to hold approximately — the atomic heats of the elements being nearly constant. The elements carbon, boron, and silicon present exceptions to this law, as Regnault had found. If the molecular heat of many compounds is divided by the number of atoms in the molecule, the quotient is approximately 6.4., *i.e.* the same as the atomic heat of the elements. The molecular heat is thus approximately the sum of the atomic heats of the atoms which are present in the molecule.

Kopp[5] drew the following general conclusions from his work: First, every element in the solid condition at a sufficient distance from its melting-point has a definite specific or atomic heat. This may vary somewhat with the temperature and density of the substance, but not very greatly. Second, every element has the same specific and atomic heat in the free condition and in combination.

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[1] *Ann. Chim. Phys.* [3], **26**, 261 (1849); **46**, 257 (1856); **63**, 5 (1861). *Compt. rend.* **55**, 887.

[2] Dumas and Stas: *Ann. Chim. Phys.* [3], **1**, 202 (1840).

[3] *Ann. Chim. Phys.* [3], **1**, 129 (1841).

[4] *Lieb. Ann. Suppl.* **3**, 1, 289 (1864–1865).

[5] *Ibid.* **3**, 289 (1864–1865).

Work of Weber. — The elements carbon, boron, and silicon presented, as we have seen, unmistakable exceptions to the law of Dulong and Petit. Weber[1] undertook to study the specific heat of these elements at different temperatures. He observed, from the work of others, that the higher the temperature the greater the specific heat found. He determined to work at higher temperatures, and found that the specific heat of carbon remained practically constant with rise in temperature, after a dull red heat was reached. Also that the specific heats of graphite and diamond became identical above 600°, and remained the same however high the temperature to which both were heated. The specific heat of carbon between 600° and 1000°, multiplied by the atomic weight of carbon (12), gave 5.4 to 5.6 as the atomic heat of carbon. The true specific heat of carbon at 2000° must be at least 0.5, so that at this temperature the atomic heat of carbon would be 6, which brings it in line with the law of Dulong and Petit.

Similar results were obtained for boron and silicon; the specific heats of these elements increased with rise in temperature to such an extent, that we are justified in concluding that the law of Dulong and Petit holds also for these elements at more elevated temperatures.

In closing this chapter on solids, we leave what we have called the *Older Physical Chemistry*. This refers not so much to the question of years as to the nature of the problems dealt with, and the methods employed in solving them. Some of the work discussed in the preceding chapters was done in the last few years, and some investigations which will be referred to in subsequent chapters were carried out early in the century. It is, however, true in general that most of the work thus far considered belongs to the period previous to 1885, and also true that a very large proportion of what follows was done subsequent to that date.

But the distinction which we wish to draw is far more fundamental than that of years. The physical chemistry of to-day differs not only in degree from that of twenty-five years ago, but in kind. What was studied and taught at that time under this head bears no close relation whatsoever to the work which is being done at present by the modern physical chemist. We have already seen what are the most characteristic features of the older physical chemistry. It was essentially the study of the physical properties of chemical substances, and the conclusions reached, as has been pointed out, were for the most part purely empirical. That they are, however, important in themselves, and especially important in what they have led to, and promise to give us in the future, no one who is familiar with the facts can deny.

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[1] *Pogg. Ann.* **154**, 367 (1875).

This phase of our subject has been dealt with at considerable length, partly because there is a marked tendency at present to disregard or ignore the work of the earlier physical chemists, and to think that physical chemistry really began about fifteen years ago. It is true that much of the older work has been temporarily obscured by the brilliancy of the newer results, but the work of men like Kopp, Bunsen, Regnault, and Stas, will ever lie at the foundation of modern science.

Having studied much of the work of the older period, we must now turn to the new physical chemistry. In the following chapter we shall show how the newer period was inaugurated. How a discovery was made about fifteen years ago, which has grown into an entirely new branch of science, a branch which already has a large literature of its own, which is being taught and studied in most of the leading universities in the world, and for which alone a number of laboratories are already equipped. The rapid growth of the science has been only commensurate with the importance of the results obtained. Modern physical chemistry has revolutionized chemical thought in many directions, it has thrown light on a number of important physical problems, and has already made its way into physiology and other branches of biology, and is now finding its way into the geological sciences.

We shall now see what are some of the more important developments of the new science.

CHAPTER V

SOLUTIONS

Kinds of Solutions. — We have dealt thus far with matter in the pure condition. A pure substance, either elementary or compound, was prepared and its properties studied. The substance might be in the gaseous, the liquid, or the solid state; or it might exist in all three states under different conditions.

We are, however, not limited to the study of matter in the pure form. One element or compound can be mixed with another element or compound, and the properties of the mixture investigated. It is not even necessary to stop here. Three or more substances might be mixed and such mixtures studied. Further, the substances which are mixed might be of the same or of different states of aggregation. Mixtures which are homogeneous, and from which the constituents cannot be separated mechanically, are termed *solutions*.

It is obvious that a number of different kinds of solutions are possible. We know matter in three distinct states of aggregation,—solid, liquid, and gas. Since matter in every state can be mixed with matter in every other state, at least theoretically, we can have nine different classes of solutions. These are: —

I. Solution of gas in gas.
II. Solution of liquid in gas.
III. Solution of solid in gas.
IV. Solution of gas in liquid.
V. Solution of liquid in liquid.
VI. Solution of solid in liquid.
VII. Solution of gas in solid.
VIII. Solution of liquid in solid.
IX. Solution of solid in solid.

It may be stated in advance that well-defined examples of all of these classes of solutions are known. Our study of solutions consists, then, essentially in a study of the properties of these nine classes of mixtures.

SOLUTIONS IN GASES

Solutions of Gases in Gases. — When different gases are brought together they either act chemically upon one another, as hydrochloric acid gas and ammonia, or they simply mix with one another, as hydrogen and nitrogen. It is to the latter class only, where no chemical action takes place, that the term "solution of one gas in another" is applied. When one gas dissolves in another, the condition is always fulfilled that any quantity of the one can dissolve in any quantity of the other. When any gas dissolves in another without acting chemically upon it, it is always soluble to an unlimited extent, and this is a characteristic of the kind of solutions with which we are now dealing.

The pressure exerted by a mixture of gases is the sum of the pressures of the constituents. This was early discovered by Dalton.[1] If we represent the pressures exerted by the constituents by $p_1, p_2, \cdots$ and the volume of the mixture by V, we have —

$$PV = V(p_1 + p_2 + \cdots).$$

This law of the summation of gas-pressures holds when the gases are not too concentrated, *i.e.* when the pressures are not great. At higher pressures many exceptions have been discovered to this generalization. Indeed, this would be expected, since, when the gas-particles are comparatively numerous in a given space, their effect upon one another would come prominently into play. It may, however, be said in general that the properties of mixtures of dilute gases are approximately the sum of the properties of the constituents.

Solutions of Liquids in Gases. — Liquids in general have the power to dissolve in gases, or, as we usually say, a liquid can send off vapor into a space containing a gas. Ordinary evaporation in the presence of the atmosphere is a phenomenon of the kind we are describing. The law of the solution of a liquid in a gas was also discovered by Dalton.[2] The vapor-pressure of the vapor of a liquid in the presence of a gas is the same as in a vacuum. A number of supposed exceptions to this law have been pointed out by Regnault[3] and others, but the recent work of Galitzine[4] on water, ethyl chloride, and ether shows that the vapor-pressure of these substances in a vacuum is very nearly the same as in the air. Some of the apparent exceptions to this law are probably due in part to a solution of the gas in the liquid with which it is in contact. This, as we shall see, lowers the vapor-tension of the liquid, and, consequently, affects the solubility of the liquid in the gas in question.

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[1] *Gilb. Ann.* **12**, 385 (1802).

[2] *Ibid.* **12**, 393; **15**, 21 (1802–1803).

[3] *Mém. Ac. Sc.* **26**, 679.

[4] *Dissertation*, Strassburg (1890).

Solutions of Solids in Gases. — There are solids known which pass over into vapor in the presence of a gas without first becoming liquid. Thus, iodine vaporizes at an elevated temperature in the presence of the atmosphere or other gases. Such mixtures are as truly solutions of solids in gases, as those which we have been considering are solutions of gases or liquids in gases. About all that is known of solutions of solids in gases is that the solubility increases with rise in temperature. This is usually expressed by saying that the vapor-tension increases with rise in temperature.

SOLUTIONS IN LIQUIDS

Solutions of Gases in Liquids. — In dealing with solutions in liquids as solvent, we must distinguish between the cases where chemical action takes place between the dissolved substance and the solvent, and where there is no chemical action. The latter constitute the true solutions in liquids.

All gases are absorbed to some extent by all liquids, the amount of gas absorbed varying greatly with the nature of the gas and also with that of the liquid. A given gas is absorbed by a given liquid to a very different extent under different conditions. It is well known that the greater the pressure to which the gas is subjected, the larger the amount dissolved. A very simple relation was discovered by Henry [1] connecting the solubility of a gas with the pressure, and which has come to be known as Henry's law. The amount of a gas dissolved by a liquid is proportional to the pressure to which the gas is subjected.

Henry tested his law for several gases at pressures ranging from one to three atmospheres, and found that it held quite closely. It has since been subjected to more careful test by Bunsen and others,[2] with the result that the law has been shown to agree very closely with the results of the best experiments.

Exceptions to the law of Henry are, however, not wanting. If the gas is very soluble in the liquid, the law does not hold. This was found by Roscoe and Dittmar [3] to be the case with ammonia in water; and similar results were obtained by Watts.[1] When the gas is very soluble in the liquid, the solution formed is concentrated. We have just seen that the law of Henry does not apply to such solutions. We shall see that practically all of the relations which have been found to hold for dilute solutions fail to hold in concentrated solutions. That Henry's law should not apply to concentrated solutions should, therefore, not be a matter of any surprise.

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[1] *Phil. Trans.* (1803). *Gilb. Ann.* **20**, 147 (1805).

[2] Khanikof and Louguinine: *Ann. Chim. Phys.* [4], **11**, 412 (1867).

[3] *Lieb. Ann.* **112**, 349 (1859).

Solutions of Liquids in Liquids. — In dealing with solutions of liquids in liquids we must distinguish sharply between two cases. First, where the liquids are infinitely soluble in each other, or, as we say, where they are miscible in all proportions, as alcohol and water. This case suggests the solution of one gas in another. Here, as we have seen, we always have infinite solubility, — gases mixing with one another in all proportions. Second, where the liquids are miscible to only a limited extent, as water and ether. Here we encounter a new condition, which we shall frequently meet with hereafter in dealing with solutions, *i.e.* limited solubility. The properties of these two classes of liquid solutions, as we shall see, are quite different. In addition to the above cases, there are liquids which are practically insoluble in one another; hence, mixtures of such liquids cannot be regarded in any true sense as solutions, since the constituents can be readily separated mechanically. There is, however, no liquid which is absolutely insoluble in any other liquid, so that the last distinction is not a sharp one.

First Class. — The properties of mixtures of liquids which mix in all proportions are not the sum of the properties of the constituents. When such liquids are mixed, there is a change in volume. Usually the volume decreases on mixing, but in some instances it increases. Changes in temperature accompany the mixing of liquids. In some cases heat is evolved; in others it is absorbed. No relation has thus far been discovered between the volume changes and thermal changes of such mixtures. Sometimes heat is evolved when there is contraction, in other cases when there is expansion in volume.

The properties of liquid mixtures, however, are often not widely different from the sum of the properties of the constituents. In such cases, where the properties of the mixture are nearly "additive," they can be approximately calculated from those of the constituents. If the volumes of the two liquids before they are mixed are v_1 and v_2, the volume of the mixture v is approximately —

$$v = v_1 + v_2.$$

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[1] *Lieb. Ann. Suppl.* **5**, 227 (1865).

One other example will suffice to illustrate this point. Take the power of liquids to refract light. If we represent the weight of the mixture by W, the index of refraction by N, and the density by D; and the corresponding values of the constituents by $w_1, w_2, w_3, \cdots$, $n_1, n_2, n_3, \cdots$, $d_1, d_2, d_3, \cdots$, the following formula was deduced by Landolt:[1]—

$$W\frac{N-1}{D}=w_1\frac{n_1-1}{d_1}+w_2\frac{n_2-1}{d_2}+w_3\frac{n_3-1}{d_3}+\cdots.$$

This formula was tested for a number of mixtures by Landolt, and found to hold. Much more recently, Schütt[2] studied the refractive power of mixtures of ethylene bromide and propyl alcohol. The index of refraction for the sodium line was represented by n for the mixture, by n_1 and n_2 for the constituents; the density of the mixture is d, that of the constituents d_1 and d_2. The percentage by weight of the one constituent is p, that of the other $100-p$:—

$$\frac{n-1}{d}=\frac{n_1-1}{d_1}\frac{p}{100}+\frac{n_2-1}{d_2}\frac{100-p}{100}.$$

Schütt tested this formula for a number of different lines in the spectrum, and found that the difference between the value calculated for the mixture and that found experimentally was about one per cent, and the difference was always on the same side. He then showed how the refractivity of one of the constituents could be calculated from that of the mixture, knowing the refractive power of the other constituent, and the percentage composition of the mixture.

We see from the above example that with mixtures such as we are now considering, the properties are never strictly "additive." They are, at best, only approximately so, and in many cases differ very considerably from the sum of the properties of the constituents.

Second Class. — A large number of liquids are known which dissolve one another to only a limited extent. The case of ether and water has already been mentioned. It is not a simple matter to calculate the properties of such mixtures from those of the constituents. One property of such mixtures, however, is especially interesting; *i.e.* the effect of temperature on the composition of the mixture. The work of Alexéew[3] has shown that salicylic acid, which melts at 156°, becomes liquid under boiling water, and when heated with water in a closed tube a little above 100°, this liquid mixes with water in all proportions. The liquid beneath the water is not molten salicylic acid, but a solution of water in salicylic acid. In the case of liquids which mix to only a limited extent, we always have two solutions formed — that of A in B, and that of B in A — if there is more of the one constituent present than will saturate the other. In the above case we have a solution of salicylic acid in water, and a solution of water in salicylic acid. These two become miscible in all proportions at a certain elevated temperature, as we have just seen. This has been found to be a general property of liquids which mix to only a limited extent. The two solutions merge into one at a temperature more or less elevated, but which can usually be realized experimentally. These facts are shown very clearly by the following curves,[1] the abscissas representing temperatures, the ordinates per cent of dissolved substance in 100 parts of solution. These curves represent aqueous solutions of phenol (1), salicylic acid (2) benzoic acid (3), aniline phenolate (4), and aniline (5). At the lower temperatures we have in each case two distinct solutions represented by the two arms of each curve. The lower arm represents the solution of the substance in water, there being relatively little substance and much water present in this solution, as is shown by the small value of the ordinate of this branch of the curve. The upper arm represents the solution of water in the substance in question, the latter being present in very large per cent, as shown by the large value of the ordinate. As the temperature rises in each case, the two arms of the curve approach, and at a certain temperature which is definite for each substance, the two arms meet. This means that at this

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[1] *Lieb. Ann. Suppl.* **4**, 1 (1865).

[2] *Ztschr. phys. Chem.* **9**, 349 (1892).

[3] *Journ. prakt. Chem.* **133**, 518 (1882); *Bull. Soc. Chim.* **38**, 145 (1882).

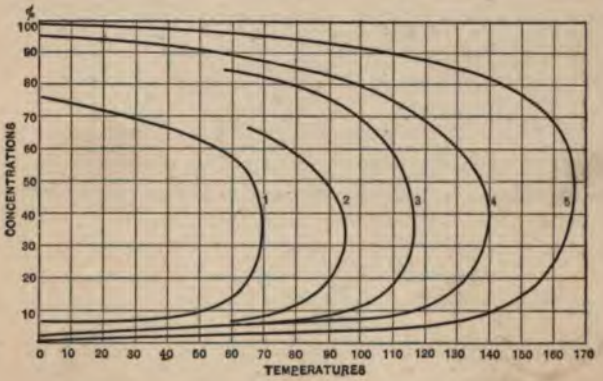

Fig. 14.

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[1] Alexéew: *Bull. Soc. Chim.* **38**, 146 (1882).

temperature the two solutions — that of A in B and that of B in A — become identical, and that the two substances can mix in all proportions.

The second class of solutions of liquids in liquids, *i.e.* those which mix to only a limited extent, can, then, be regarded as a special condition of the first class, which mix in all proportions. The condition is, that ordinary temperatures are below that at which such liquids would mix in all proportions. When solutions of liquids which belong to the second class are heated up to a certain temperature, they become miscible in all proportions, and, consequently, pass over into solutions of the first class.

Vapor-pressure, Boiling-point, and Distillation of Liquid Mixtures. — I. If the liquids do not mix to any appreciable extent, each exerts its own vapor-pressure independent of the other liquids which may be present. The vapor-pressure is, then, the sum of the vapor-pressures of the liquids which are brought in contact with one another. This has been verified experimentally by Regnault.[1] A few of his results are given in the following table: —

TEMPERATURE	WATER	CARBON BISULPHIDE	SUM	VAPOR-PRESSURE OF MIXTURE
12°.07	10.5 mm.	216.7 mm.	227.2 mm.	225.9
26°.87	26.3 mm.	388.7 mm.	415.0 mm.	412.3

The differences here are less than one per cent, the sum of the separate pressures being slightly greater than the vapor-pressure of the mixture. This is just what we would expect, since each liquid is slightly soluble in the other, and, as we shall see, would therefore slightly lower the vapor-pressure of the other liquid. Similar results were obtained by Regnault for other pairs of liquids which dissolve one another to only a slight extent.

Such mixtures as the above would necessarily boil lower than the lowest boiling constituent, since the vapor-pressures of the several constituents summate, and would overcome the pressure of the atmosphere at a temperature lower than that at which the lowest boiling constituent alone would overcome it.

The vapors of such mixtures would contain all of the constituents, and in the same proportions as the relative vapor-pressures of the liquids present. When such mixtures are distilled, the distillate would contain all of the liquids present. The quantity of each would depend upon the relative vapor-pressures at the temperature of distillation. Some exceptions to this simple rule have been discovered.

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[1] *Pogg. Ann.* **93**, 537 (1854).

II. If the liquids are partly miscible, the vapor-pressure of the mixture is less than the sum of the vapor-pressures of the constituents at the same temperature. This, again, is what we would expect, since each liquid present would depress the vapor-tension of the other. In these cases it is not possible to say offhand just what the boiling-point would be. It generally lies below the boiling-point of the lowest boiling constituent, but it can be coincident with it, or even higher than this temperature. The position of the boiling-point of the mixture with respect to that of the constituents would be conditioned largely by the degree of solubility of each liquid in the other. If the liquids readily dissolved one another, there would be a considerable depression of the vapor-tension of each by the other, and, consequently, the mixture would boil higher; if, on the other hand, the liquids were only slightly soluble in each other, there would be relatively little depression of the vapor-tensions, and the mixture would boil lower; in this case, lower than the lowest boiling constituent.

When such mixtures are distilled, the product contains all of the constituents. The composition of the product remains constant as long as there are two layers present, since each solution has its own definite vapor-pressure at a given temperature. The effect of distillation would be to diminish the lower boiling solution more rapidly than the higher boiling. While there were two solutions present the boiling-point would remain constant, and would change only when one of the layers disappeared.

Konowalow[1] has studied the products of distillation of such mixtures, and has plotted his results in curves. The abscissa represents percentage of alcohol; the ordinate, vapor-pressure. The following curves represent the results for a mixture of water and isobutyl alcohol.

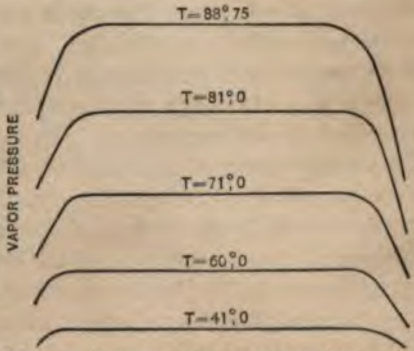

FIG. 15. PERCENTAGE ISOBUTYL ALCOHOL.

Konowalow measured the vapor-pressures of the mixtures at different temperatures. The results in the above table of curves were obtained between 41° and 88°.75. While the alcohol present was not sufficient to saturate the water, the vapor-pressure of the solution increased with increase in alcohol. This is shown by the rise in the curve. When the water became saturated with the alcohol, the vapor-pressure became constant and independent of the excess of alcohol present. Such a mixture has a constant boiling-point, and the distillate a constant composition. When the excess of alcohol present becomes so large that all the remaining water present can dissolve in it, the vapor-pressure again changes with the composition, as is shown by the fall in the curve. The vapor-pressure finally falls to the value for pure alcohol.

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[1] *Wied. Ann.* **14**, 34 (1881).

If the mixture represented by any point on the straight line is distilled, the composition of the vapor and the boiling-point will remain constant. But if a mixture represented by any point on either the rising or falling arm of the curve is distilled, the composition of the vapor and the boiling-point will change gradually, until the liquid which is present in relatively large quantity will remain behind in nearly pure condition.

III. If the liquids are soluble in one another in all proportions, the vapor-pressure of the mixture is always less than the sum of the vapor-pressures of the constituents at the same temperature. This follows of necessity from the fact that a dissolved substance lowers the vapor-pressure of the solvent. The composition of the vapor given off from such mixtures bears no close relation to the composition of the mixture. The vapor contains a preponderating amount of the most volatile constituent. Upon this fact rests the possibility of separating such mixtures by fractional distillation.

It is difficult to say at once where such mixtures will boil with respect to the boiling-points of the constituents. We have seen that the vapor-pressure of such a mixture is never equal to the sum of the vapor-pressures of the constituents. It may lie between the sum and the higher or lower vapor-pressure of the constituents; or it may even fall below the pressure of the constituent which has the lowest vapor-pressure. The boiling-point of such mixtures would, of course, vary inversely as the vapor-pressures, and, consequently, no general relation between the boiling-points of such mixtures and those of the constituents can be established.

When such mixtures are distilled, that constituent which has the highest vapor-pressure (lowest boiling-point) tends to pass over in largest quantity. By repeating the distillation, it is, therefore, possible to obtain the lowest boiling constituent in nearly pure condition. Konowalow[1] studied the composition of the vapor and the vapor-pressure at different temperatures, of mixtures of liquids which mix in all proportions. The following curves were plotted from his results: —

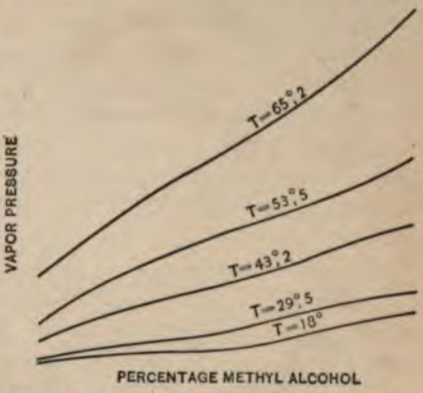

FIG. 16. WATER AND METHYL ALCOHOL.

The curves for methyl alcohol and water, and ethyl alcohol and water, show that as the amounts of alcohol increase, the vapor-pressure increases. The curves show no sign of any maximum or minimum of vapor-pressure, and since the tendency is for that substance to pass over first which has the greatest vapor-pressure, the lowest boiling substance will pass over in nearly pure condition, since, as is seen at once from the curves, the vapor-tension increases as this substance becomes greater and greater. Mixtures such as methyl alcohol and water, and ethyl alcohol and water, can then be separated by fractional distillation. All mixtures whose vapor-tension curves are of this type (Figs. 16 and 17), *i.e.* do not have maxima or minima, can be separated more or less completely by fractional distillation.

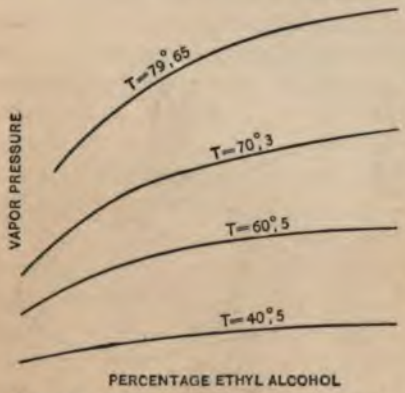

FIG. 17. WATER AND ETHYL ALCOHOL.

Mixtures with Constant Boiling-point. — Konowalow[2] also studied mixtures of water and propyl alcohol, and water and formic acid. His results are plotted in the following curves: —

The curves for mixtures of water and propyl alcohol at different temperatures all show a maximum of vapor-tension, when there is about 70 per cent of the alcohol present. This mixture, containing about 30 per cent of water, has a greater vapor-pressure than any other mixture of these two substances. This mixture will, then, have the lowest boiling-point of any possible mixture of water and propyl alcohol; and if we distil any mixture of these substances, the distillate will tend more and more to the composition of this mixture. If we repeat the distillation several times, we shall obtain finally, not pure water or pure propyl alcohol as the distillate, but the mixture having the maximum vapor-tension, and, consequently, the lowest boiling-point.

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[1] *Wied. Ann.* **14**, 34 (1881).

[2] *Loc. cit.*

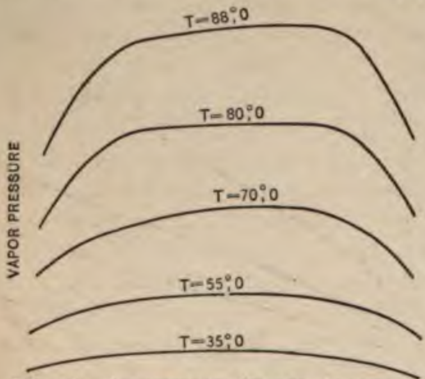

Fig. 18. Percentage Propyl Alcohol.

The curves for formic acid and water, instead of showing a maximum of vapor-tension show a minimum. This minimum exists when the mixture contains about 75 per cent of formic acid. A mixture of this composition has, then, a lower vapor-tension than any other mixture of water and formic acid, and, consequently, a higher boiling-point. If any mixture of these two substances is distilled, the composition of the residue will approach more and more nearly to that of the mixture having the lowest vapor-tension, and by repeated distillation we can finally obtain a residue in the flask which corresponds very closely to this composition.

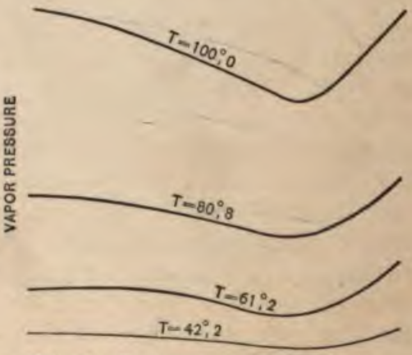

Fig. 19. Percentage Formic Acid.

It is obvious that mixtures which show a maximum or minimum vapor-tension cannot be separated into their constituents by fractional distillation. Instead of obtaining the pure substances, a mixture will be obtained, in the one case in the distillate having a maximum vapor-tension, in the other in the residue having a minimum vapor-tension.

Such mixtures with constant boiling-points have long been known, and were once supposed to be definite chemical compounds. A mixture of 20.2 per cent of hydrochloric acid and water has a constant boiling-point, 110°, at the pressure of the atmosphere, and can be distilled without change in composition. Similarly, a mixture containing 68 per cent of nitric acid in water has a constant boiling-point, and many others are known.

Roscoe[1] has proved that these mixtures are not definite chemical compounds, by showing that the composition of the distillate changed when the distillation was effected under different pressures. Thus, when a mixture of hydrochloric acid and water was distilled under a pressure of two atmospheres, the mixture which had a constant boiling-point contained 19 per cent of the acid, instead of 20.2 per cent as when the distillation was carried on under a pressure of one atmosphere.

There is, then, not the slightest reason for regarding these mixtures with constant boiling-points as chemical compounds.

Solutions of Solids in Liquids. — Whenever a solid is brought into the presence of a liquid, some of the solid dissolves. This is perfectly general; for, as we shall see, even metallic platinum dissolves to a slight extent in water. When we consider the number of solids and liquids known, it is evident that the number of such solutions is almost infinite. Indeed, we have become so accustomed to solutions of this class, that when the term "solution" is used, we think first of the solution of a solid in a liquid solvent. The most striking characteristic, perhaps, of solutions of solids in liquids is that there is a limit to the solubility of every solid in any liquid. We know of no solid which dissolves to an unlimited extent in any liquid. The degree of solubility, however, varies greatly. Some of the more resistant metals, like gold, platinum, etc., are so nearly insoluble in neutral liquids, that the most refined chemical methods are incapable of detecting their presence in the solvent, and only the most refined physical and physical chemical methods can show that they have any solubility whatever. The solubility of some compounds, on the other hand, is very great indeed. We should mention especially the strontium and calcium salts of permanganic acid. These have recently been prepared in quantity by Morse and Black,[2] using the beautiful method of preparing permanganic acid devised by Morse and Olsen,[3] and their solubility in water determined. One part by weight of water at 18° dissolves 2.9 parts of strontium permanganate and 3.31 parts of calcium permanganate. Yet even in such extreme cases as these, a limit is reached, and beyond this it is impossible to go. That point at which a liquid cannot take up more of the solid at a given temperature is known as the point of *saturation*, and such a solution is known as a *saturated solution*.

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[1] *Lieb. Ann.* **116**, 203 (1860).

[2] Dissertation, Johns Hopkins Univ. (1900).

[3] *Amer. Chem. Journ.* **23**, 431 (1900).

There are two general methods of preparing saturated solutions. The substance, say a salt, is brought in contact with the solvent and the two shaken together at a constant temperature, until the liquid will take up no more of the salt. This is theoretically very simple, but it is found in practice that the time required to fully saturate a solution in this way is in some cases very great indeed.

Another method which has been employed is based upon the fact that the solubility of many substances increases with rise in temperature. If it is desired to saturate a solvent at a given temperature, it is heated to a somewhat higher temperature and shaken with the substance to be dissolved. The amount which is readily dissolved at the higher temperature is more than sufficient to saturate the solution at the lower temperature. When the solution is cooled down to the desired temperature, any excess of the dissolved substance will separate out in the presence of some undissolved substance, and the solution will be saturated at the required temperature. While the results obtained by the first method are generally a little too low, due to the incomplete saturation of the solution, those obtained by the second are generally a little too high, since all of the excess of substance in solution may not separate unless the solution is vigorously stirred, and brought freely in contact with some of the undissolved substance. In studying saturated solutions it is best to use both methods, and take the mean between the results of the two.

Just as we may have solutions which can take up more of the dissolved substance and are, therefore, *unsaturated*, so we may have solutions which contain more of the dissolved substance than corresponds to a state of stable equilibrium. Such solutions which are in a state of unstable equilibrium are termed *supersaturated*. If a supersaturated solution is shaken with some of the undissolved substance, the excess of substance in solution will be deposited, and the supersaturated will become a saturated solution. We thus have a ready means of distinguishing between these three conditions of solutions. If the solution can take up more of the dissolved substance at a given temperature, it is unsaturated at that temperature. If, when brought in contact with some of the undissolved substance it neither dissolves more of the substance nor deposits any of that already in solution, it is a saturated solution. If in contact with some of the undissolved substance it deposits some of the substance already in solution, it is a supersaturated solution. Supersaturated solutions are formed most readily by salts which crystallize with water of crystallization. A number of anhydrous salts can also form supersaturated solutions.

The general effect of *temperature* on solubility has been indicated. The solubility of most substances in most solvents increases with rise in temperature. This, however, is not always true. In some cases solubility decreases with rise in temperature. The best examples are found among the salts of the organic acids, and of these we should mention especially the calcium salts. When a saturated solution of a calcium salt, say of citric acid, is heated to a higher temperature than that at which it was saturated, some of the salt in solution is deposited as a precipitate. When the solution cools again the precipitate redissolves. Similar results are obtained with salts of other metals and other acids. The decrease in solubility with rise in temperature is well illustrated by some of the cyanides. Much work has been done on the properties of solutions in liquids as solvents, and some of the most important results in physical chemistry have been obtained in this field. We shall now take up at some length the more important of these investigations, and show the bearing of some of the results obtained, and conclusions which have been reached.

OSMOTIC PRESSURE

Osmotic Pressure. — If a solution of a substance in a solvent is placed in a vessel, and over this solution the pure solvent is poured, we shall find after a time that the substance is not all contained in that part of the solvent in which it was originally present, but a part of it has passed into the layer of the pure solvent which was poured upon the solution. This shows that there is some force analogous to a pressure, driving the dissolved substance from one region to another, from the more concentrated to the less concentrated solution. This pressure has been termed *osmotic pressure.*

Demonstration of Osmotic Pressure. — The existence of this pressure was early recognized. Abbé Nollet demonstrated its existence about the middle of the eighteenth century. A glass tube closed at the bottom with animal parchment was filled with ordinary alcohol, and the tube then immersed in water. Water could pass in through this parchment, but alcohol could not pass out. The contents of such a tube gradually increased in volume, showing to the eye the existence of osmotic pressure. During the first three-fourths of the last century osmotic pressure was demonstrated by filling an animal bladder with an aqueous solution of alcohol and immersing the bladder in water. The water passed into the bladder and the alcohol could not pass out in any quantity. Hence, the bladder became distended and finally burst. It will be observed that in all of these experiments recourse was had to animal membranes. A discovery was subsequently made which has entirely done away with the use of natural membranes in demonstrating osmotic pressure.

These membranes, which have the property of allowing the solvent to pass through them, and of preventing the dissolved substance from passing, are known as *semi-permeable*. It was M. Traube[1] who first prepared such semi-permeable membranes artificially. He found that certain precipitates, deposited in a suitable manner, have the property of allowing the solvent to pass through them, but hold back the dissolved substance. These precipitates include copper ferrocyanide, and a number of similar gelatinous substances. A good method of demonstrating osmotic pressure, now that we can prepare artificial membranes, is the following. A glass tube about 2 cm. in diameter and 8 to 10 cm. long, is tightly closed at the bottom with vegetable parchment. This is soaked in water for some hours so as to drive out air-bubbles. The top of the glass tube is tightly closed with a rubber stopper, through which is passed a fine capillary tube about a metre in length. The end of the capillary should just pass through the cork, but must not protrude beyond its lower surface. The large glass tube is now immersed in a beaker which is sufficiently deep to receive the entire tube. The tube is then firmly clamped in a vertical position. The beaker is filled with a three per cent solution of copper sulphate. The cork is then removed from the tube, and the latter completely filled with a three per cent solution of potassium ferrocyanide, to which enough potassium nitrate has been added to make from a one to a two per cent solution. The tube is then closed as tightly as possible with the cork through which the capillary passes, care being taken that no air-bubble remains beneath the cork. The apparatus is then set in a quiet place for some days. After a day or two, if the experiment is successful, the liquid will begin to rise in the capillary, and may reach a height of from 40 to 50 cm.

The experience of the writer has been that not all such experiments succeed. Indeed, the number which give a good demonstration of osmotic pressure is only about one-third of the total attempts which he has made. The frequent failure is doubtless due in part to the nature of the parchment used.

The method by which the semi-permeable membrane is formed in this case is almost self-evident. The copper sulphate from below passes into the parchment, and the potassium ferrocyanide from above also enters the parchment. The two meet right in the walls of the vegetable parchment. At the surface of contact they form the gelatinous precipitate of copper ferrocyanide in the walls of the parchment. The precipitate, deposited in this manner, has the property of semi-permeability — it allows the water to pass through and prevents the dissolved substances from passing. Since osmotic pressure always acts so that water passes from the more dilute to the more concentrated solution, the flow of water in this case is from the copper sulphate on the outside to the potassium ferrocyanide and potassium nitrate on the inside. The liquid rises in the capillary due to the inflow of water through the semi-permeable membrane.

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[1] *Archiv f. Anat. und Physiol.*, p. 87 (1867).

Morse's Method of measuring Osmotic Pressure. — The measuring of osmotic pressure has now become a very simple matter, due to a method devised in this laboratory by Morse, and developed by Morse and Horn.[1] They state the object they had in mind in the following words: —

"It occurred to the authors that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall. The results of our experiments in this direction appear to have justified the expectation."

In order to remove the air contained in the walls of the cup they made use "of the strong *endosmose* which appears when a current is passed through a porous wall separating two portions of a dilute solution in which the two electrodes are immersed." A dilute boiled solution of potassium sulphate was used for this purpose. "On passing the current between the electrodes in the direction of the one within the cup, the liquid in the cup rises with a rapidity which increases with the dilution of the solution, and with the intensity of the current. The water, in passing through the wall, appears to sweep out the air in an effective manner."

Having removed the air by means of endosmosis, the membrane was formed by filling the cup with a tenth-normal solution of potassium ferrocyanide, and immersing it in a tenth-normal solution of copper sulphate. One electrode of platinum was inserted into the cup, and the other of sheet copper completely surrounded the cup. The current was passed from the copper to the platinum electrode. As soon as the copper ions, moving with the current, come in contact with the $Fe(CN)_6$ ions moving against the current, a precipitate of copper ferrocyanide was formed within the wall[1] of the cup. This gradually became more compact, as was shown by the fact that the resistance offered to the passage of the current rapidly increased.

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[1] *Amer. Chem. Jour.* **26**, 80 (1901).

The advantage of driving the ions into the wall by means of the current is that the membrane can be formed much more compactly than by simply allowing them to pass into the wall by diffusion. With such a cell it is possible to demonstrate osmotic pressure in a most satisfactory manner. When the cell is filled with a normal solution of cane sugar, closed with a cork through which a capillary manometer passes, and immersed in pure water, the liquid will rise in the capillary at the rate of more than a foot an hour, and in one day a pressure of thirty feet of the sugar solution is easily secured. This so far surpasses all other demonstrations of osmotic pressure thus far devised, that they become insignificant by comparison. The demonstration of osmotic pressure on the lecture table by means of this method has become as simple a matter as many of the daily experiments in inorganic and organic chemistry.

This method promises much for the quantitative study of osmotic pressure. The ease with which the cells can be prepared, and the great resistance offered by the membranes formed by the electrical method, bid fair to open up new possibilities in connection with the direct measurement of osmotic pressure. As the method was devised less than a year ago, it has not yet been possible to make extensive quantitative applications of it. *Pressures of 31.5 atmospheres* have, however, been measured. Work along this line is now in progress.

Measurement of Osmotic Pressure. — The most accurate quantitative method of measuring osmotic pressure thus far applied has been devised and used by W. Pfeffer.[2] He made use of the artificial membranes which had been discovered by Traube, and deposited them upon a support which was sufficiently resistant to enable them to withstand considerable pressure. An account of the apparatus used by Pfeffer and the method which he employed will be given in his own words:[3] "I obtained the first favorable results by proceeding as follows: I took [*unglazed*] porcelain cells, such as are used for electric batteries, and, after suitably closing them, I first injected them carefully with water, and then placed them in a solution of copper sulphate, which, either immediately or after a short time, I introduced into the interior of a solution of potassium ferrocyanide. The two membrane-formers now penetrate diosmotically the porcelain wall separating them, and form, where they meet, a precipitated membrane of copper ferrocyanide. This appears, by virtue of its reddish brown color, as a very fine line in the white porcelain which remains colorless at all other places, since the membrane, once formed, prevents the substances which formed it from passing through.

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[1] In very hard-burned cups the membrane forms on the inner surface of the cup.

[2] *Osmotische Untersuchungen.* Leipzig, 1877.

[3] *Ibid.* pp. 4–6, 7–8, 20. Scientific Memoirs Series, IV, 4–5. Edited by Prof. J. S. Ames. (Published by Amer. Book Co.)

"In Fig. 1 the apparatus ready for use, with the manometer (*m*) for measuring the pressure, is shown, at approximately one-half the natural size.

"The porcelain cell *z* and the glass pieces *v* and *t*, inserted in position, are shown in median longitudinal section. The porcelain cells which I used were on the average, approximately 46 mm. high, were about 16 mm. internal diameter, and the walls were from 1¼ to 2 mm. thick. The narrow glass tube *v*, called the connecting-piece, was fastened into the porcelain cell with fused sealing-wax, and the closing-piece *t* was set into the other end of this tube in the same manner. The shape and purpose of this are shown in the figure."

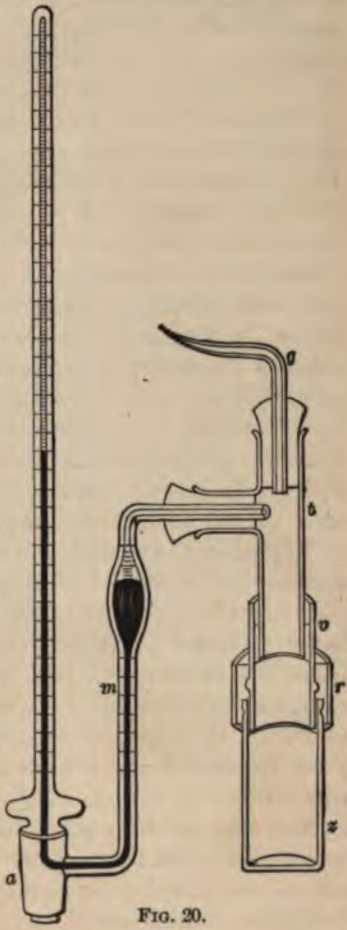

FIG. 20.

To give some idea of the great number of details which must be followed out in order to prepare a good cell for measuring osmotic pressure the following paragraphs are quoted from Pfeffer's monograph: —

"All[1] porcelain cells were treated first with dilute potassium hydroxide, and then with dilute hydrochloric acid (about 3 per cent), and after being well washed were again completely dried before they were closed, as already described. Substances which are soluble in these reagents, such as oxides and iron, which under certain conditions can do harm, would thus be removed.

"After the apparatus was closed the precipitated membrane was formed either in the wall or upon the surface, according to the principle already indicated. In order that this should be done successfully, a number of precautionary measures are necessary, and these will now be discussed. Since I experimented chiefly with membranes of copper ferrocyanide, which were deposited upon the inner surface of porcelain cells, I will fix attention especially upon this case.

"The porcelain cells were first completely injected with water under the air-pump, and then placed for at least some hours in a solution containing 3 per cent of copper sulphate, and the interior was also filled with this solution. The interior of the porcelain cell was then rinsed out once quickly with water, well dried as quickly as possible by introducing strips of filter paper, and after the outside had dried off somewhat, it was allowed to stand some time in the air until it just felt moist. Then a 3 per cent solution of potassium ferrocyanide was poured into the cell, and this immediately reintroduced into the solution of copper sulphate.

"After the cell had stood for from twenty-four to forty-eight hours undisturbed, it was completely filled with the solution of potassium ferrocyanide and closed as shown in Fig. 1. A certain excess of pressure of the contents of the cell now gradually manifested itself, since the solution of potassium ferrocyanide had a greater osmotic pressure than the solution of copper sulphate. After another twenty-four to forty-eight hours the apparatus was again opened, and generally a solution introduced which contained 3 per cent of potassium ferrocyanide and 1½ per cent of potassium nitrate, and which showed an excess of osmotic pressure of somewhat more than three atmospheres."

If all of these details are carefully observed and suitable fine-grained porcelain cells are chosen, the preparation of good semi-permeable membranes offers no serious difficulty. Pfeffer states that he prepared twenty such cells almost without a failure.

The measurements of osmotic pressure were made by means of these porcelain cells lined with the precipitate which formed the semi-permeable membrane. After the manometer was attached to the cell, the latter was filled with the solution whose osmotic pressure was to be measured. The cell was then tightly closed and fastened to a glass rod as seen in figure.

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[1] Scientific Memoirs Series, IV, 6–7. Edited by Ames (Amer. Book Co.).

The whole cell, including the manometer, was introduced into a bath as shown in the figure. The bath was filled with pure water, and the osmotic pressure of the solution against pure water measured on the mercury manometer. Special precautions were taken to keep the temperature of the whole apparatus constant, since, as we shall see, there is a large temperature coefficient of osmotic pressure. The temperature of the experiment was accurately determined by means of carefully standardized thermometers.

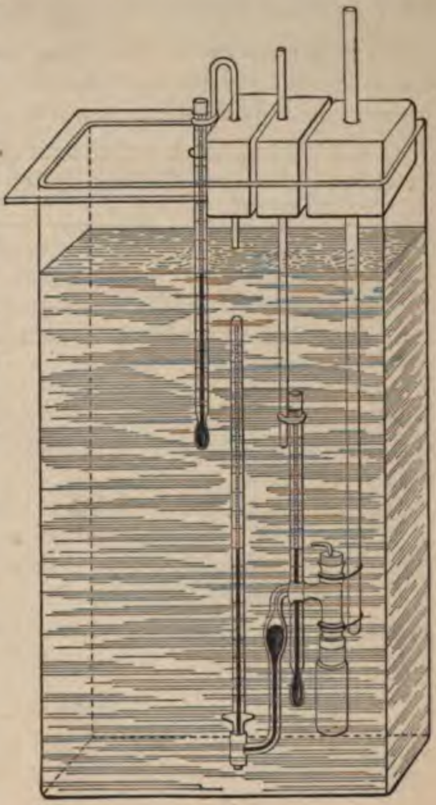

Fig. 21.

Some of Pfeffer's Results. — Pfeffer measured the osmotic pressure of solutions of a number of substances at different concentrations. With cane sugar he obtained the following results for dilutions ranging from one to six per cent, keeping the temperature as nearly constant as possible. The temperature for the series ranged from 13°.5 to 14°.7.

C = Concentration in Per Cent by Weight[1]	P Osmotic Pressure	$\frac{P}{C}$
1 per cent	53.5 cm.	53.5
2 per cent	101.6 cm.	50.8
4 per cent	208.2 cm.	52.0
6 per cent	307.5 cm.	51.2

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[1] *Osmotische Untersuchungen* (1877), p. 110.

From these results it would appear that osmotic pressure is proportional to the concentration of the solution, since $\frac{P}{C} =$ a constant, or very nearly a constant. The deviation from a constant is so slight that it is evidently due to experimental error. The following results were obtained with potassium nitrate: —

C = Concentration in Per Cent by Weight[1]	P Osmotic Pressure	$\frac{P}{C}$
0.80 per cent	130.4 cm.	163.0
1.43 per cent	218.5 cm.	152.8
3.3 per cent	436.8 cm.	132.4

The ratio of pressure to concentration decreases as the concentration increases in this case. These results are, however, not very accurate, since the membrane used by Pfeffer was not entirely impervious to potassium nitrate.

Pfeffer also studied the effect of temperature on osmotic pressure. He took a given solution and measured its osmotic pressure at different temperatures, and in this way worked out the temperature coefficient of osmotic pressure. The following results were obtained with a one per cent solution of cane sugar: —

Temperature	Osmotic Pressure
6°.8	50.5 cm.
13°.2	52.1 cm.
14°.2	53.1 cm.
22°.0	54.8 cm.
36°.0	56.7 cm.

It is obvious from these results that the osmotic pressure of such a solution increases with rise in temperature.

Similar results were obtained with sodium tartrate: —

Temperature	Osmotic Pressure
13°.3	147.6 cm.
36°.6	156.4 cm.

Effect of the Nature of the Membrane on Osmotic Pressure. — The effect of the nature of the semi-permeable membrane on the magnitude of the osmotic pressure was also investigated by Pfeffer.[2] In addition to copper ferrocyanide, he used membranes of Berlin blue and calcium phosphate. It will be observed that all of these substances are gelatinous precipitates like copper ferrocyanide. Pfeffer found an osmotic pressure of only 38.7 cm. for a one per cent solution of cane sugar when Berlin blue was used as the membrane, and only 36.1 cm. when calcium phosphate was employed. From these results it would seem at first sight that the nature of the membrane had an influence on the magnitude of the osmotic pressure. The real explanation of these differences is, however, quite different. The membranes of Berlin blue and calcium phosphate were not sufficiently resistant to withstand the pressure, consequently they would leak, and the true value of the maximum pressure was never shown by the manometer. This conclusion was made very probable by the behavior of these membranes during the experiments. Of all the membranes tried by Pfeffer, only copper ferrocyanide was capable of withstanding the pressure, and only those results which were obtained with this membrane can be regarded as the true expressions of the osmotic pressures of the solutions employed.

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[1] *Osmotische Untersuchungen*, p. 113.

[2] *Ibid.* p. 116.

Further, Ostwald[1] has devised an ingenious method for proving theoretically that the osmotic pressure of a solution is independent of the nature of the membrane used in measuring it. Given the cylinder, Fig. 22.

Introduce two semi-permeable membranes, M_1 and M_2, as shown in the drawing. The space between the membranes contains the solution, the two spaces, A and B, the pure solvent. Let us first suppose that the osmotic pressure at M_1 is greater than at M_2. Let us call the first pressure p_1, and the second pressure p_2. The solvent will pass in through both membranes until the pressure p^2 is reached. Then the solvent will cease to flow in through M_2, but will continue to enter through M_1. As soon as the pressure in the solution between the membranes exceeds p_2, the solvent will flow out through the membrane M_2, and will continue to flow in through M_1. Since the pressure could, then, never rise to p_1, the solvent will continue to flow in through M_1 forever, and to flow out through M_2. We would thus have perpetual motion, which is impossible. Suppose we assume, on the other hand, that p_2 is greater than p_1, by an exactly similar line of reasoning it is shown that we would then have a continual flow of the solvent through the cylinder from right to left — the reverse of

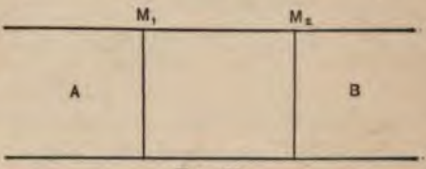

Fig. 22.

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[1] *Lehrb. d. Allg. Chem.* I, p. 662.

the first direction. Again, we would have perpetual motion, which is impossible. Therefore, since p_1 cannot be greater nor less than p_2, it must be equal to it. In a word, the osmotic pressure of a solution is independent of the nature of the membrane used in measuring it.

It is, of course, assumed in this discussion that the dissolved substance is such as would not act chemically upon the membrane. If there was any chemical action, the membrane would be destroyed at once and the experiment ruined.

The quantitative measurements of the absolute osmotic pressure of solutions made by Pfeffer are the best up to the present. Indeed, very little has been done along this line since Pfeffer ended his work. We should, however, mention in this connection the work of Adie.[1]

Measurement of the Relative Osmotic Pressures of Solutions. — While but little work has been done recently on the absolute osmotic pressures of solutions, probably on account of the difficulties involved in such work, much has been done on the relative osmotic pressures exerted by different substances. A number of new methods have been devised for measuring relative osmotic pressures, and some of these, together with the results obtained, we shall now consider.

Method employing Vegetable Cells. — The method is based upon the preparation of solutions of different substances, each of which will have the same osmotic pressure as the contents of cells of certain plants; and, therefore, the same osmotic pressure as one another. The difficulty is to determine just when the solution around the cell has the same osmotic pressure as the contents of the cell itself. This has been accomplished by the Dutch botanist De Vries,[2] to whom the method with which we shall now deal is due. He found three plants which fulfil the conditions necessary to success, — *Tradescantia discolor*, *Curcuma rubricaulis*, and *Begonia manicata*. The cells of these plants are four to six sided. The cell-walls are strong and resistant, and do not change their size or shape when the cell is immersed in solutions of other substances. These walls are easily permeable to water and aqueous solutions. The cell-walls are lined on the inside with a very thin, colorless membrane, which is filled with the colored contents of the cell. This membrane is semi-permeable, allowing water to pass, but holding back the dissolved substance. The contents of the cell is an aqueous solution of glucose, potassium and calcium malate, coloring matter, etc., having an osmotic pressure of from four to six atmospheres. The semi-permeable membrane lining the cell-wall distends when the contents of the cell increases in volume, and contracts when the volume of the contents diminishes.

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[1] *Chem. News*, **63**, 123 (1891). *Proc. Chem. Soc.* 344 (1891).

[2] *Ztschr. phys. Chem.* **2**, 415 (1888).

The method of determining the relative osmotic pressure of the contents of the cell and of the solution in which it is placed will be readily understood from the foregoing description of the cell. Thin tangential sections are taken from the middle rib on the under side of the leaf of *Tradescantia*[1] containing a few hundred living cells. This section is placed under the microscope, and the cells surrounded by the solution whose osmotic pressure it is desired to compare with that of the contents of the cells. In such a preparation, all of the cells have the same osmotic pressure, since any differences would have equalized themselves in the plant. It is then only necessary to compare the osmotic pressure of the solution with that of any one of the cells present.

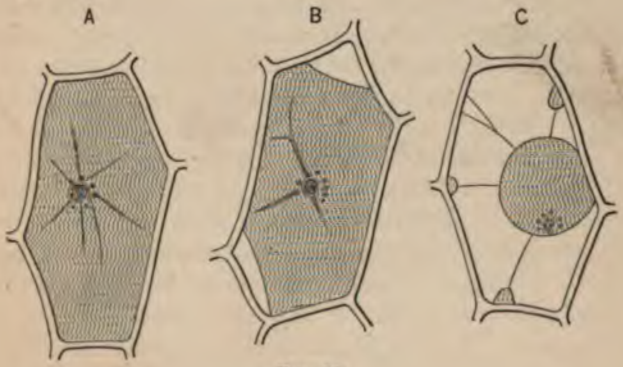

FIG. 23.

When the cell is immersed in a solution having the same osmotic pressure as the contents of the cell, the cell has the normal appearance as shown in *A* in the figure. When the cell is immersed in a solution having a smaller osmotic pressure than its own contents, it will also have the appearance of *A*, in the figure. Water will pass from the solution through the semi-permeable membrane into the cell, and tend to distend it. But the resistant cell-wall will prevent any appreciable distention, and, consequently, the cell will appear about as a normal cell. If, on the other hand, the cell is immersed in a solution having greater osmotic pressure than its own contents, water will pass from the cell through the membrane out into the solution. The cell contents, having lost water, will contract as shown in *B* and *C* in the figure; the semi-permeable membrane will also contract and follow the cell contents, and this contraction can readily be seen since the cell contents are colored. By starting with a solution whose osmotic pressure is greater than that of the cell, shown by the contracting of the cell contents when the cell is surrounded by the solution, and continually diluting it, noting its action on the cell at every stage of dilution, a solution is finally reached in which the cell will just preserve its normal form. The solution then has the same osmotic pressure as the contents of the cell. The solution can then be analyzed and its strength determined. In an exactly similar manner solutions of other substances can be prepared, each having the same osmotic pressure as the contents of the cell, and these solutions analyzed and their strengths determined. Since each of these solutions has the same osmotic pressure as the contents of the cell, they have the same osmotic pressure. This method can, of course, be applied only to those substances which do not act chemically on the delicate membranes which surround such plant cells. This method has been called by De Vries the *plasmolytic*. He[1] determined the concentrations of quite a large number of substances which were isosmotic with the cell contents. These isosmotic or isotonic concentrations were expressed in gram-molecular quantities, and their reciprocal values were termed the *isotonic coefficients* of the substances. These isotonic coefficients show at once the relative osmotic pressures of solutions of equal molecular concentration. The isotonic coefficient of potassium nitrate is taken as 3. A few of De Vries' results are given for future reference.

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[1] Cells are taken from other places in different plants.

SUBSTANCE	FORMULA	ISOTONIC COEFFICIENT
Glycerol	$C_3H_8O_3$	1.78
Invert sugar	$C_6H_{12}O_6$	1.81
Cane sugar	$C_{12}H_{22}O_{11}$	1.88
Malic acid	$C_4H_6O_5$	1.98
Tartaric acid	$C_4H_6O_6$	2.02
Citric acid	$C_6H_8O_7$	2.02
Potassium nitrate	KNO_3	3.00
Sodium chloride	$NaCl$	3.05
Potassium acetate	$C_2H_3O_2K$	3.00
Calcium chloride	$CaCl_2$	4.33
Magnesium chloride	$MgCl_2$	4.33
Potassium citrate	$C_6H_5O_7K$?	5.01

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[1] *Ztschr. phys. Chem.* **2**, 427 (1888); **3**, 103 (1889).

An examination of these results shows certain relations which we shall learn are very important. The neutral organic substances and the weak organic acids have isotonic coefficients which are about constant, and which have the value of approximately 2. The salts have much higher coefficients — ranging from 3 to 5. The meaning of these facts will appear in due time.

Method employing Animal Cells. — We have seen above how vegetable cells can be used to measure relative osmotic pressures. We can use certain cells of animals for the same purpose. Hamburger[1] has used the red blood corpuscles of the deer and frog. If to defibrinated deer's blood a solution of potassium nitrate, 1.04 per cent, is added, the red blood corpuscles will settle completely to the bottom and will be covered by a clear, almost colorless liquid. If the solution of potassium nitrate has a concentration of 0.96 per cent, or less, the separation into the two layers is not complete. The corpuscles do not settle to the bottom completely, and, consequently, the supernatant liquid is somewhat colored — the more deeply colored the more dilute the solution of potassium nitrate added. By proceeding carefully, a solution of potassium nitrate can be found in which the red corpuscles will just settle to the bottom. Similarly, solutions of other substances can be prepared of such a concentration that the red blood corpuscles will just settle and leave a clear liquid above them. Such solutions have the same osmotic pressure; and from these data it is evident that the isotonic coefficients of substances can be calculated, as from the results obtained by De Vries using vegetable cells. Without giving the results of Hamburger in detail, it may be stated that the isotonic coefficients which he found, agree with those obtained by De Vries to within the limits of error of the two methods. Reference only can be made to the work of others,[2] in which red blood corpuscles were used.

Method in which Bacteria are used. — We have seen how both vegetable and animal cells can be used to determine relative osmotic pressure. We shall now see that cells which are neither the one nor the other, or perhaps both, can also be used in this connection. Wladimiroff[3] has used certain forms of bacteria, such as *Bacterium Zopfii*, *Bacillus subtilis*, *Bacillus Typhi abdominalis*, *Spirillum rubrum*, etc. The movements of the bacteria were found to be very different in solutions of the same substance of different concentrations. If we start with a very dilute solution and continually increase its strength, the movements of the bacteria become slower and slower. Solutions of different substances were prepared of such strengths that they had the same influence on a given kind of bacteria, and then their relative concentrations determined. The conclusions reached by Wladimiroff were, that although certain neutral salts seem to have a poisonous action on some bacteria, and certain salts could enter the protoplasm of other bacteria, yet most of the relations investigated between salts and bacteria agreed with the laws of osmosis as established by entirely different methods.

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[1] *Ztschr. phys. Chem.* **6**, 319 (1890).

[2] W. Loeb: *Ibid.* **14**, 424 (1894). H. Koppe: *Ibid.* **16**, 261 (1895). S. G. Hedin: *Ibid.* **17**, 164; **21**, 272 (1895 and 1896).

[3] *Ibid.* **7**, 529 (1891).

Method of Tammann.—It still remains to describe a method which differs fundamentally from the three just considered. In these three methods the semi-permeable membrane was of living substance. The semi-permeable membrane in the optical method is an inorganic precipitate and, indeed, the same precipitate as was used by Pfeffer in preparing his porcelain cells. If a drop of a solution of potassium ferrocyanide is allowed to fall into a solution of copper sulphate, the drop becomes completely surrounded with a precipitate of copper ferrocyanide, and this precipitate, as we have seen, forms the very best semi-permeable membrane. We would have, then, a drop of a solution of potassium ferrocyanide surrounded by a semi-permeable membrane, and this in contact with a solution of copper sulphate. If the solution of potassium ferrocyanide is more dilute than that of copper sulphate, water will pass out into the copper sulphate, dilute it just around the drop, and, consequently, produce a current of the more dilute solution upward from the drop. If, on the contrary, the contents of the drop are more concentrated than the solution of copper sulphate, water will pass from the copper sulphate through the membrane into the solution of potassium ferrocyanide. The solution of copper sulphate just around the drop will thus become more concentrated, and because of its greater specific gravity, will sink to the bottom. It is, then, only necessary to observe whether the current rises or falls from the drop, to determine the relative concentrations of the two solutions. In these observations a refractometer is used, slight currents being detected by the different refractivities. It is, of course, possible to prepare the two solutions of such concentrations that water will pass neither the one way nor the other. The two solutions would then have the same osmotic pressure. It is thus quite possible to prepare solutions of ferrocyanides which are isosmotic with copper and zinc salts. The work of Tammann,[1] who devised this method, was limited to these substances. It has, however, been extended more recently to a third substance added to the other two, provided the third substance does not act chemically upon either of the others. This method is obviously subject to narrower limitations than any of those previously considered; the methods involving the use of living membranes being applicable to all substances which do not act upon the cells and destroy them.

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[1] *Wied. Ann.* **34**, 299 (1888).

A careful study of the best methods available for measuring osmotic pressure will undoubtedly leave the impression that this is a quantity with which it is difficult to deal experimentally. While it is possible to prepare good cells according to the method worked out by Pfeffer, yet much time and experience are necessary to secure fair results. And further, the best that has been accomplished up to the present is to measure the osmotic pressure of comparatively dilute solutions. Pfeffer's work was limited to a six per cent solution of cane sugar, — less than one-fifth normal, — and no one has since been able to work at greater concentrations. To determine the absolute osmotic pressure of more concentrated solutions, it is evident that some indirect method must be applied, since thus far it has been scarcely possible to prepare membranes which shall be able to withstand, without rupture, a pressure of many atmospheres. It should be stated again that the method of Morse, already described, promises much in this direction.

Relations have, however, been established between the osmotic pressure of solutions and certain other properties which can be readily dealt with experimentally. As we shall see, by measuring certain other quantities we can easily calculate the osmotic pressure of solutions which are far too concentrated, and whose osmotic pressures are far too great to measure directly. These matters will be further discussed in the proper places.

RELATIONS BETWEEN OSMOTIC PRESSURE AND GAS-PRESSURE

Pfeffer carried out the measurements already referred to, and doubtless saw their physiological significance, but he did not point out any relations between osmotic pressure and gas-pressure. This, like so many other brilliant discoveries, was reserved for Van't Hoff. In his epoch-making paper,[1] which has contributed more toward the development of the new physical chemistry than any other one article, he points out a number of surprisingly simple relations, and some of these will now be taken up.

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[1] *Ztschr. phys. Chem.* **1**, 481 (1887). Scientific Memoirs Series, IV, p. 13.

Boyle's Law for Osmotic Pressure. — The law of Boyle for gases states that the pressure of a gas varies directly as the concentration of the gas. We have seen from Pfeffer's results, that the osmotic pressure of a solution varies directly with the concentration. This is shown by the fact that $\frac{P}{C}$ is a constant, to within the limits of experimental error. This relation for the osmotic pressure of solutions certainly suggests the relation for gases expressed by the law of Boyle.

Van't Hoff also points out that the work of De Vries leads to the same conclusion. De Vries took solutions of potassium nitrate, potassium sulphate, and cane sugar, and determined the concentrations which were isosmotic or isotonic with the contents of a given cell. He then used cells of other plants and determined the isosmotic concentrations of these substances. Four such isotonic series were worked out. The results are given below, the concentrations being expressed in gram-molecules per litre, the unit being potassium nitrate.

Series	KNO_3	K_2SO_4	$C_{12}H_{22}O_{11}$
I	1	0.75	—
II	1	0.77	1.54
III	1	0.77	1.54
IV	1	—	1.54

The relation between the concentrations which have the same osmotic pressure is constant, independent of the actual value of the concentrations. This is but another expression of the law of Boyle as applied to the osmotic pressure of solutions.

Gay-Lussac's Law for Osmotic Pressure. — According to the law of Gay-Lussac the pressure of a gas increases with the temperature, at the rate of $\frac{1}{273}$ for every rise of one degree centigrade. Pfeffer's results show that the osmotic pressure of a solution increases with rise in temperature, and the rate of increase is very nearly $\frac{1}{273}$ for every degree. Pfeffer did not make an extensive study of the temperature coefficient of osmotic pressure, but as far as his results go they lead to the conclusion stated above. If we examine the effect of temperature on osmotic pressure, as shown on page 186, we shall see that this conclusion is, in general, confirmed.

If the law of Gay-Lussac applies to the osmotic pressure of solutions, then solutions which are isosmotic at one temperature must remain isosmotic at other temperatures, since they would have the same temperature coefficient of osmotic pressure. This has been tested by the methods for determining relative osmotic pressures. Hamburger, using the method already referred to as involving red blood corpuscles, found that solutions of potassium nitrate, sodium chloride, and cane sugar, which were isosmotic at 0°, were also isosmotic at 34°.

There is, however, a still more striking experimental verification of the applicability of the law of Gay-Lussac to solutions. If a tube is filled with a gas and all parts of the tube kept at the same temperature, the concentration of the gas will be the same in every part of the tube. If, on the other hand, one portion of the tube is kept warmer than the others, the gas will so distribute itself throughout the tube that the pressure will remain the same in all parts of the tube. Since the pressure of a gas increases with the temperature, each particle will exert a greater pressure in the warmer region, and, consequently, there will be fewer particles required in the warmer portion of the tube to exert the same pressure as exists in the colder portion. In a word, the gas would tend to become more concentrated in the colder portion, and more dilute in the warmer portion of the tube.[1]

If the osmotic pressure of solutions obeys the laws of gas-pressure, a phenomenon similar to the above should be observed with solutions, and such is the fact. If the two parts of a perfectly homogeneous solution are kept at different temperatures for any considerable length of time, the solution becomes more concentrated in the region which is colder. This has come to be known from its discoverer as the *principle of Soret*.[2] This principle is of the very greatest importance in testing the law of Gay-Lussac for osmotic pressure. If this law holds, then the colder portion of the solution should become more concentrated by $\frac{1}{273}$ for every difference of one degree in temperature. This could be easily tested by experiment. The experiments were carried out by Soret by placing the solutions in vertical tubes, in such a manner that the upper portions of the tubes were warmed to a constant temperature, and the lower portions cooled to a constant temperature. The earlier experiments of Soret gave a

[1] It should, of course, be remembered that the condition described for a gas is somewhat ideal. The gas particles, due to their rapid movement, would mix, but the principle which it is desired to illustrate holds good.

[2] *Ann. Chim. Phys.* [5], **22**, 293 (1881).

difference in concentration which was not quite as great as that calculated from the law of Gay-Lussac. His later experiments, in which the solutions were allowed to stand at constant temperatures for a longer time, gave differences which, while a little too low, yet accorded very nearly with the theory. A slight difference between calculated and experimental values creates no surprise when we consider that the solutions must stand for months at the constant temperatures in order that equilibrium may be reached, and some mixing of the parts due to agitation or jarring is, therefore, unavoidable. The agreement is, however, so close that it is now quite certain that the principle of Soret furnishes the best proof of the applicability of the law of Gay-Lussac to the osmotic pressure of solutions.

Avogadro's Law applied to the Osmotic Pressure of Solutions. — The applicability of the laws of Boyle and Gay-Lussac to the osmotic pressure of solutions, shows that this quantity is analogous to gas-pressure. It, however, leaves the question as to the relative magnitudes of the two pressures entirely unanswered. The one might be very large and the other very small, and still the two laws which we have just considered apply to both. We now come to the question, is there any close relation between the magnitudes of the two pressures exerted under comparable conditions?

The law of Avogadro, applied to gases, states that in equal volumes of all gases at the same temperature and pressure, there are the same number of ultimate parts. If the law of Avogadro applied to solutions it would be stated thus, in equal volumes of solutions which, at the same temperature have the same osmotic pressure, there are contained the same number of dissolved particles. The simplest way in which this law can be tested for solutions is to see what relation exists between the gas-pressure of a gas particle and the osmotic pressure of a dissolved particle under the same conditions of temperature and concentration. Let us compare the gas-pressure of hydrogen gas and the osmotic pressure of cane sugar in water. Given a one per cent solution of cane sugar; such a solution would contain one gram of sugar in 100.6 cc. of water, and the osmotic pressure of such a solution can be calculated from Pfeffer's results. Hydrogen gas, having the same number of parts in a given volume, would have the following pressure: The molecular weight of cane sugar is 342, that of hydrogen 2. The hydrogen gas must, therefore, contain $\frac{2}{342}$ grams in 100.6 cm., which is the same as 0.0581 grams per litre. Hydrogen gas at 0°, and at a pressure of one atmosphere, weighs per litre 0.08995 grams; the above concentration of hydrogen gas will, therefore, exert a gas-pressure of $\frac{0.0581}{0.08995} = 0.646$ atmosphere at 0°.

It is now only necessary to compare the osmotic pressure exerted by the cane sugar with this gas-pressure, to see if any simple relations exist between the two. The following table of results is taken from the paper by Van't Hoff:[1]—

Temperature	Osmotic Pressure of Cane Sugar	Gas-pressure of Hydrogen Gas
6°.8	0.664	0.665
13°.7	0.691	0.681
15°.5	0.684	0.686
36°.0	0.746	0.735

The remarkable fact is established by these results that *the osmotic pressure of a solution of cane sugar is exactly equal to the gas-pressure of a gas having the same number of parts in a given volume*, temperature being the same in both cases. Under the same conditions, then, a dissolved particle exerts the same osmotic pressure as a gas particle exerts gas-pressure.

Causes of Gas-pressure and of Osmotic Pressure. — That there should be an equality between these two pressures is very surprising, if we consider the great difference between the phenomena with which we are dealing. Gas-pressure is explained in terms of the kinetic theory of gases, as due to the particles of gas bombarding against the walls of the confining vessel. It should be stated that we do not know what is the cause of osmotic pressure. A great number of explanations and theories have been offered to account for osmotic pressure, but in the opinion of the writer no one of them is at all satisfactory. Some have attempted to account for osmotic pressure by the attraction of water by the dissolved substance, but this is only a renaming of the phenomenon, and in no sense an explanation of it. Others have suggested that water passes through the semi-permeable membrane from the more dilute to the more concentrated solution, because of the screening action of the dissolved particles. These cannot pass through the membrane, and, therefore, screen it from the blows of the solvent. Since the greater screening influence is exerted on the side containing the larger number of dissolved particles, we have the flow of the solvent from the more dilute to the more concentrated solution. A careful analysis of this explanation shows that it is not sufficient. The screening influence of the dissolved particles would be just as great below, keeping the water which has passed through the membrane from rising, as it is above, since the membrane is quite permeable to water. It is, therefore, fairest to say that we have at present no satisfactory theory to account for that phenomenon known as osmotic pressure.

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[1] *Ztschr. phys. Chem.* **1**, 493 (1887).

Exceptions to the Applicability of the Gas Laws to Osmotic Pressure. — We have just seen that the three best known laws of gas-pressure apply to the osmotic pressure of solutions of substances like cane sugar. We might conclude from this that the laws of gas-pressure always apply to the osmotic pressure of solutions of all substances. Such is not the case. Van't Hoff[1] pointed out that there are not only exceptions to this generalization, but a great many exceptions. Indeed, the substances which present exceptions are quite as numerous as those which conform to the rule. The osmotic pressure of most salts, of all the strong acids, and all the strong bases, is much greater for all concentrations than would be expected from the osmotic pressure of solutions of substances like cane sugar for the same concentrations. The osmotic pressures of these three classes of substances are always greater than would be expected from the laws of gas-pressure applied to the osmotic pressure of solutions.

The general expression for the laws of Boyle and Gay-Lussac is, as we have seen (page 45) —

$$pv = RT.$$

This applies directly to the osmotic pressure of solutions of substances like cane sugar. But in order that it may apply to solutions of salts, acids, and bases, a coefficient must be introduced, which, for these substances, is always greater than unity. This coefficient was called by Van't Hoff i, and it has come to be known as the Van't Hoff i.

The above expression when applied to acids, bases, and salts becomes —

$$pv = iRT.$$

While these exceptions were clearly recognized by Van't Hoff, he was unable to explain them, or to offer any satisfactory theory to account for them.

In this case, as in so many others, the exceptions are as interesting and important as the cases which conform to rule. We shall see that these exceptions led to a theory which is one of the most important in modern chemical science, and which, together with the relations between gas-pressure and osmotic pressure just considered, constitutes the corner-stone of modern physical chemistry.

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[1] *Ztschr. phys. Chem.* 1, 501 (1887).

The paper which we have just considered is of such fundamental importance that it is difficult to lay too much stress upon it. As the subject develops we shall see its bearing at every turn, and shall learn to regard it as, indeed, epoch-making in the highest sense,—as a monumental contribution to science in the last part of the nineteenth century.

It is always of interest to follow the line of thought which leads to any great discovery. The steps by which Van't Hoff was brought in contact with the work of Pfeffer on osmotic pressure, and was led to the study of dilute solutions from this standpoint, were developed in full by Van't Hoff in a lecture before the German Chemical Society in 1894, and which appeared in the *Berichte*, Vol. **27**, 6. A brief account of this lecture was given by the present writer in his *Theory of Electrolytic Dissociation*, p. 77.

ORIGIN OF THE THEORY OF ELECTROLYTIC DISSOCIATION

The Problem as it was left by Van't Hoff. — Van't Hoff saw clearly, as we have stated, that a large class of compounds shows an osmotic pressure which conforms to the gas laws, and yet a very large class gives an osmotic pressure which is always too great. Van't Hoff's own words in this connection will be given:[1] "If we are still considering 'ideal solutions,' a class of phenomena must be dealt with which, from the now clearly demonstrated analogy between solutions and gases, are to be classed with the earlier so-called deviations from Avogadro's law. As the pressure of the vapor of ammonium chloride, for example, was too great in terms of this law, so, also, in a large number of cases, the osmotic pressure is abnormally large, and in the first case, as was afterwards shown, there is a breaking down into hydrochloric acid and ammonia, so also with solutions we would naturally conjecture that in such cases a similar decomposition had taken place. Yet it must be conceded that anomalies of this kind existing in solutions are much more numerous, and appear with substances which it is difficult to assume break down in the usual way. Examples in aqueous solutions are most of the salts, the strong acids, and the strong bases. . . . It may then have appeared daring to give Avogadro's law for solutions such a prominent place, and I should not have done so had not Arrhenius pointed out to me, by letter, the probability that salts and analogous substances when in solution break down into ions."

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[1] *Ztschr. phys. Chem.* **1**, 500 (1887). Scientific Memoirs Series, IV, 34. Edited by Ames (Amer. Book Co.).

The last sentence furnishes the connecting link between the generalization reached by Van't Hoff and the discovery of the theory of electrolytic dissociation. The latter we owe to the Swedish physicist Arrhenius, to whose work we shall now turn.

Work of Arrhenius. — A paper bearing the title *On the Dissociation of Substances Dissolved in Water* appeared in the same volume of the *Zeitschrift für physikalische Chemie*[1] as the paper by Van't Hoff, which we have just considered. Arrhenius was impressed by the generalizations reached by Van't Hoff connecting gas-pressure and osmotic pressure, and especially by the large number of exceptions to these generalizations. Referring to the equality of gas-pressure and osmotic pressure under the same conditions, Arrhenius says:[2] "Van't Hoff has proved this law in a manner which scarcely leaves any doubt as to its absolute correctness. But a difficulty which still remains to be overcome is that the law in question holds only for 'most substances,' a very considerable number of the aqueous solutions investigated furnishing exceptions, and in the sense that they exert a much greater osmotic pressure than would be required from the law referred to."

Arrhenius stated the problem in the above words. We will now follow the line of thought which led him to its solution.[2]

"If a gas shows such a deviation from the law of Avogadro, it is explained by assuming that the gas is in a state of dissociation. The conduct of chlorine, bromine, and iodine, at higher temperatures, is a very well-known example. We regard these substances under such conditions as broken down into simple atoms.

"The same expedient may, of course, be made use of to explain the exceptions to Van't Hoff's law; but it has not been put forward up to the present, probably on account of the newness of the subject and the many exceptions known, and the vigorous objections which would be raised from the chemical side to such an explanation."

Arrhenius then puts forward the assumption of the dissociation of certain substances dissolved in water to explain the exceptions to Van't Hoff's generalization. Osmotic pressure is, as we have seen, proportional to the concentration of the solution. This is the same as to say that osmotic pressure is proportional to the number of dissolved particles. If a substance exerts an abnormally great osmotic pressure, there must be more parts present in the solution than we would expect from the concentration. But acids, bases, and salts, represented by hydrochloric acid, potassium hydroxide, and potassium chloride, are the substances which show the abnormally great osmotic pressure. How is it possible to conceive of substances such as these breaking down into any larger number of parts than would correspond to their molecules?

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[1] *Ztschr. phys. Chem.* 1, 631 (1881). Scientific Memoirs Series, IV, p. 47.

[2] Scientific Memoirs Series, IV, 47–48. Edited by Ames (Amer. Book Co.).

This is the problem which must be solved, and Arrhenius has solved it, as we believe, satisfactorily. He went back to the theory proposed by Clausius to account for the facts which were known in connection with the phenomenon of electrolysis. The theory of Clausius will be developed later at some length. Suffice it to say here that it was found that an infinitely weak current will decompose water to which a little acid is added, liberating hydrogen at one pole and oxygen at the other. If the aqueous solution of the acid contained only molecules, in order that we might have electrolysis the current must be capable of decomposing the molecules. The fact is that a current far too weak to decompose a molecule of water will effect electrolysis. Therefore, some of the molecules present in the solution, either those of the water or of the acid, must be already broken down before the current is passed. Clausius did not claim that the molecules are broken down into their constituent atoms. Such a theory would be absurd. His theory was that the molecules are broken down into parts, which he called *ions*, and each ion is charged with electricity, either positively or negatively. An ion may be a charged atom or a charged group of atoms.

The theory that molecules are broken down into ions by a solvent like water was proposed, then, by Clausius in 1856.

A similar theory was advanced by the chemist Williamson in 1851, as the result of his work on the synthesis of ordinary ether from alcohol and sulphuric acid. This, also, will be considered in detail in the proper place. The theory of Clausius differed from that of Williamson, in that the former assumed that there are only a few molecules broken down into ions, while Williamson thought that most of the molecules present are in a state of decomposition. It should be observed that both of these theories are purely qualitative suggestions. The one thought that only a few molecules in solution are broken down into ions, the other, that we have to do mainly with ions; but neither suggested any method by which we could determine the actual amount of the dissociation in any case.

The new feature which was introduced by Arrhenius was to point out a method for determining just what per cent of the molecules is broken down into ions. He thus converted a purely qualitative suggestion into a quantitative theory, which could be tested experimentally. The methods for measuring the amount of dissociation in solution, which were worked out by Arrhenius, will be considered in the proper places. It would be premature to discuss them here, since they fall naturally in line in the subsequent chapters.

The Theory of Electrolytic Dissociation. — The theory of electrolytic dissociation, as we have it to-day, states that when acids, bases, and salts are dissolved in water, they break down or dissociate into ions. Examples of the three classes are the following: —

$$HCl = \overset{+}{H} + \overset{-}{Cl},$$

$$KOH = \overset{+}{K} + \overset{-}{OH},$$

$$KCl = \overset{+}{K} + \overset{-}{Cl}.$$

Each compound dissociates into a positively charged part called a *cation*, and a negatively charged part an *anion*. These ions may be charged atoms as the above cations, or groups of atoms as the anion OH. The cations are usually simple atoms charged with positive electricity. The cation of all acids is hydrogen; the nature of the anion varies with the nature of the acid. It may be chlorine, bromine, the NO_3 group, SO_4, etc. The anion of bases is the group (OH); the cation varies with the nature of the base. It may be potassium, barium, ammonium, etc. The anions and cations of salts both vary with the nature of the salt. They depend upon the nature of the acid and the base which have combined to form the salt.

It was stated that hydrogen is the cation into which all acids dissociate. It may be added that this is the characteristic ion of all acids, and whenever it is present we have acid properties. Further, we never have acid properties unless there are hydrogen ions present. The same may be said of the hydroxyl ions into which bases dissociate. This is the characteristic ion of bases.

The evidence bearing upon the theory of electrolytic dissociation, and the objections which have been urged to it, will be presented as the subject develops. One misconception which has arisen so often must, however, be anticipated in advance.

It has been repeatedly urged that the theory claims that a compound like potassium chloride dissociates into potassium and chlorine, and since neither potassium nor chlorine can remain in the presence of water under ordinary conditions without acting upon it, the theory is self-evidently wrong. This objection, like so many others, is based upon an imperfect understanding of the theory. No one has ever claimed that a compound like potassium chloride dissociates in the presence of water yielding atomic or molecular potassium, having the properties of ordinary potassium. The products of dissociation are a potassium ion and a chlorine ion, and the potassium ion is a potassium atom charged with a unit of positive electricity. There is no reason whatever for supposing any close agreement between the general properties of a potassium atom and those of a potassium atom charged with electricity. About the only property which we would expect to remain unchanged is that of mass, and the mass of an atom is not changed by charging it. The properties of atoms are doubtless very closely connected with the energy relations which obtain in or upon the atom. When we change these as fundamentally as by adding an electrical charge, we would expect fundamental changes in properties; and such are the facts. It can be safely stated that whatever may be the ultimate fate of the theory of electrolytic dissociation, it will never suffer seriously from any such objection as that just referred to.

LOWERING OF THE FREEZING-POINTS OF SOLVENTS BY DISSOLVED SUBSTANCES

Blagden; **Rüdolph**; **Coppet**. — It was early known that a dissolved substance lowers the freezing-point of the solvent in which it is dissolved. The best illustration which we have of this fact in nature is the sea. Salt water freezes lower than pure water. Here, as in so many other cases, qualitative observation preceded quantitative measurement by a long time. Near the close of the last century certain relations were discovered between the quantity of dissolved substance and the amount by which the freezing-point of water was lowered. It was pointed out by Blagden[1] that the freezing-point lowering is proportional to the amount of dissolved substance, and this has come to be known as the Law of Blagden. This law, as we know to-day, is by no means general. In some cases it holds approximately, while in many cases the lowering increases more slowly than the amount of substance as the concentration of the solution increases. As a first attempt at a generalization in this field the law of Blagden is important.

The same relation was discovered much later by Rüdolph,[2] who was not aware of the work which had been done by Blagden.

[1] *Phil. Trans.* **78**, 277 (1788).

[2] *Pogg. Ann.* **114**, 63 (1861); **116**, 55 (1862).

An important advance was made in the study of the freezing-point lowering of solvents by dissolved substances by Coppet.[1] Instead of working with percentage concentrations he used quantities of different substances which were comparable. He used molecular quantities of substances, and expressed his concentrations in terms of gram-molecules of the substance in a given quantity of the solvent. He expressed the freezing-point lowerings in terms of gram-molecular concentrations, and used the term which has since come so much to the front — molecular lowering of the freezing-point. Coppet carried out fairly extensive investigations, and pointed out a number of relations such as the approximate equality of the molecular lowering produced by analogous substances. His method, of course, did not compare in accuracy with that used in subsequent work, and, therefore, his results will not be considered in any detail.

Work of Raoult. — The work of Raoult[2] on the lowering of the freezing-point is really epoch-making in this field, and has furnished the incentive for much of the best work which has been subsequently done. He used a number of solvents and studied the lowering of their freezing-points produced by a number of different kinds of chemical substances. In working with aqueous solutions he used not only acids, bases, and salts, but also a large number of organic compounds. By thus widely extending the field of cryoscopic measurements he was able to point out a number of relations which had hitherto been undiscovered.

A few of the many results obtained by Raoult will be given, and then some of his conclusions from his investigations.

He represents by A the lowering of the freezing-point produced by one gram of substance in one hundred grams of the solvent, and by M the molecular weight of the compound. The molecular lowering, $T, = MA$.

"I have found that if the solutions are dilute . . . all the organic substances in aqueous solution produced a molecular lowering which is nearly constant . . . and I have shown[3] what use could be made of this fact for determining the molecular weights of organic compounds soluble in water. I will now show that analogous results are obtained with all solvents which can be readily solidified, and that a very important general law is connected with them."

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[1] *Ann. Chim. Phys.* [4], **23**, 366 (1871); **25**, 502 (1872); **26**, 98 (1872).

[2] *Ibid.* [5], **28**, 137 (1883); [6], **2**, 66 (1884). Scientific Memoirs Series, IV, 71.

[3] Scientific Memoirs Series, IV, 71. Edited by Ames (Amer. Book Co.). *Ann. Chim. Phys.* [5], **28**, 137 (1883).

SOLUTIONS IN ACETIC ACID

SUBSTANCE	FORMULA	MOLECULAR LOWERING
Methyl iodide	CH_3I	38.8
Carbon bisulphide	CS_2	38.4
Ether	$C_4H_{10}O$	39.4
Acetone	C_3H_6O	38.1
Potassium acetate	$C_2H_3O_2K$	39.0
Sulphuric acid	H_2SO_4	18.6
Hydrochloric acid	HCl	17.2
Magnesium acetate	$C_4H_6O_4Mg$	18.2

The molecular lowerings in acetic acid centre around two values, viz. 39 and 18 — the one being double the other.

SOLUTIONS IN BENZENE

SUBSTANCE	FORMULA	MOLECULAR LOWERING
Methyl iodide	CH_3I	50.4
Nitrobenzene	$C_6H_5NO_2$	48.0
Ether	$C_4H_{10}O$	49.7
Ethyl formate	$C_3H_6O_2$	49.3
Acetone	C_3H_6O	49.3
Arsenic trichloride	$AsCl_3$	49.3
Methyl alcohol	CH_4O	25.3
Ethyl alcohol	C_2H_6O	28.2
Benzoic acid	$C_7H_6O_2$	25.4

Here, also, we find that the molecular lowering centres around the two values, 49 and 25.

The results obtained with water as a solvent are more irregular than in any other case. This is the reason why the earlier experimenters in this field failed to discover generalizations. They all worked with aqueous solutions, and with aqueous solutions of metallic salts. Raoult was the first to employ organic compounds with water as a solvent.

The same relations discovered with other solvents appear also

SOLUTIONS IN WATER

SUBSTANCE	FORMULA	MOLECULAR LOWERING
Hydrochloric acid	HCl	39.1
Nitric acid	HNO_3	35.8
Sulphuric acid	H_2SO_4	38.2
Potassium hydroxide	KOH	35.3
Sodium hydroxide	$NaOH$	36.2
Potassium formate	HCO_2K	35.2
Sodium sulphate	Na_2SO_4	35.4
Sodium oxalate	$Na_2C_2O_4$	43.2
Calcium nitrate	$Ca(NO_3)_2$	37.4
Copper sulphate	$CuSO_4$	18.0
Methyl alcohol	CH_4O	17.3
Glycerol	$C_3H_8O_3$	17.1
Acetone	C_3H_6O	17.1
Malic acid	$C_4H_6O_5$	18.7
Hydrocyanic acid	HCN	19.4
Ammonia	NH_3	19.9

here. The molecular lowerings in water centre roughly around the two values, 37 and 18.5. All the salts of the alkalies and all the salts of the strong acids and bases give a molecular lowering of approximately 37. Some salts of the bivalent metals, all the weak acids and bases, and all the organic compounds give a molecular lowering of approximately 18.5.

Conclusions from the Work of Raoult. — Raoult drew the following conclusions from his investigations: —

"Every substance, solid, liquid, or gaseous, when dissolved in a definite liquid compound capable of solidifying, lowers its freezing-point.

"The molecular lowerings of the freezing-points of all the solvents, produced by the different compounds dissolved in them, approach two mean values which vary with the nature of the solvent, the one being twice the other."[1]

Raoult points out clearly how it is possible to use the lowering of the freezing-point to determine the molecular weight of the dissolved substance. The substances which produce the lower or the higher value belong to well-defined groups, and this fact can be made use of in determining molecular weights. Thus, the salts of the alkalies in water give a molecular lowering of about 37. We must, therefore, take that molecular weight of the salt which, when multiplied by the coefficient A gives 37. If we are dealing with organic compounds, we must adopt that molecular weight which, when multiplied by A gives 18.5. Other solvents can be employed, and the molecular weights of the dissolved substances determined in a number of solvents. The importance of the freezing-point method in determining molecular weights will be taken up a little later; reference is made to it here to show that it is the direct outcome of the work of Raoult, and that the possibility of determining the molecular weights of substances in solution was clearly pointed out by him.

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[1] Scientific Memoirs Series, IV, 88–89. Edited by Ames (Amer. Book Co.).

Raoult's Law for Different Solvents. — If the molecular lowerings of the different solvents are divided by the molecular weights of the solvents, the law of Raoult becomes apparent. The table for six solvents, taken from the paper by Raoult,[1] is given below: —

	M MOLEC. WEIGHT	L MOLEC. LOWERING	$\frac{L}{M}$ OR LOWERING PRODUCED BY 1 MOLECULE IN 100 MOLECULES
Water . . .	18	47	2°.61
Formic Acid . .	46	29	0°.63
Acetic Acid . .	60	39	0°.65
Benzene . .	78	50	0°.64
Nitrobenzene . .	123	73	0°.59
Ethylene bromide .	188	119	0°.63

With the exception of water, the value of $\frac{L}{M}$ *is very nearly a constant, independent of the nature of the solvent.* Raoult points out that this is, indeed, not surprising; since, if the lowering of the freezing-point is so largely independent of the nature of the dissolved substance, as we know that it is, why should it not also be independent of the nature of the solvent?

Leaving water out of the question for a moment, the general law of the lowering of the freezing-point of solvents, as discovered by Raoult, can be formulated thus: —

"If one molecule of any substance is dissolved in one hundred molecules of any liquid of a different nature, the lowering of the freezing-

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[1] *Loc. cit.*

point of this liquid is always nearly the same, and approximately 0°.63."[1]

Exception presented by Water. — The exception to this law presented by water is quite interesting in the light of what we have already learned with respect to the state of aggregation of the molecules of pure water. From a study of the surface-tension of water, it will be remembered that Ramsay and Shields came to the conclusion that there are four chemical molecules of water aggregated to form what is sometimes called the physical molecule. In other words, the formula for the molecule of water in the liquid state should be $(H_2O)_4$ or H_8O_4.

An examination of the preceding table for aqueous solutions will show that the maximum molecular lowering for water may be as great as 49, and a number of cases are known where it is as great as 47. This is just about the value which we would expect, if the molecules of water were aggregated in groups of four: —

$$\frac{47}{18 \times 4} = 0.65.$$

This value is very close to the mean of the values found for the other five solvents.

The conclusion reached by Ramsay and Shields, from a study of the surface-tension of water, is thus confirmed by the freezing-point lowerings produced by dissolved substances.

It should be stated before leaving the law of Raoult that the most refined work has subsequently shown that the law is not rigidly true. It is only an approximation to the truth, but one which coördinates a large number of otherwise more or less disconnected facts.

Freezing-point Lowering and the Dissociation Theory. — According to the theory which had just been proposed by Arrhenius, acids, bases, and salts in the presence of water are broken down into parts, which were called ions. Solutions of these substances, it will be remembered, gave a greater osmotic pressure than would be expected from the concentrations employed. Just these same substances gave a too great lowering of the freezing-point of water. If the compound was of the type of hydrochloric acid, potassium hydroxide, or potassium chloride, *i.e.* such as would dissociate into two ions, the molecular lowering in dilute solutions was nearly twice as great as the normal. If the molecule of the substance could dissociate into three ions, as sulphuric acid, barium hydroxide, or barium chloride, the molecular lowering was nearly three times the normal, if the solutions were dilute.

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[1] Scientific Memoirs Series, IV, 92. Edited by Ames (Amer. Book Co.).

These facts accord perfectly with the results of the measurements of osmotic pressure, and furnish strong evidence in favor of the theory of electrolytic dissociation — an ion lowering the freezing-point to the same extent as a molecule.

Arrhenius[1] saw the significance of these facts in connection with his theory, and pointed out that we have here a method of testing the theory. He used the freezing-point method to determine the values of the coefficient i, which had been introduced by Van't Hoff into the general gas equation, in order that it might be applied to the osmotic pressure of solutions. Arrhenius pointed out that the value of i could be obtained by the freezing-point method as follows: If a gram-molecular weight of a non-dissociated compound is dissolved in a litre of water, the lowering of the freezing-point of the water is 1°.85. If the substance is dissociated, the lowering produced by a solution of equal concentration is always greater than the above. In order to find the value of i, it is only necessary to divide the molecular lowering found, $t°$, by 1.85: —

$$i = \frac{t}{1.85}.$$

Arrhenius determined by this method the value of i for a large number of substances, and compared the values obtained with those found by another method, which we will consider later. It was from this comparison, as we shall see, that the theory of electrolytic dissociation at once came into prominence.

Apparatus devised by Beckmann. — The measurements of the freezing-points of solvents and of solutions, which had been made up to this time, were necessarily not very refined. Neither the apparatus employed nor the method used admitted of any very high degree of accuracy. An important step toward the improvement of both method and apparatus was taken by Beckmann,[2] after a number of attempts had been made by Hentschel[3] and others. The apparatus designed and used by Beckmann is shown in the following figure: —

The glass vessel A is to receive the solvent or solution whose freezing-point is to be determined. The substance can be introduced through the side-tube, but the latter can be readily dispensed with. The tube A passes through a cork into the wider glass tube A_1, and an air-space exists between the walls of the two tubes. The thermometer T is inserted into A, and fastened tightly in position by means of a cork. The liquid in A is stirred by means of a glass rod bent in a circle of sufficient diameter to allow the bulb of the thermometer to pass through. The stirrer is attached to a vertical rod S, and moved up and down by means of the hand. B is a battery jar, which contains the freezing-mixture. The substance used in the jar depends upon the freezing-point of the solvent with which we are dealing. If the solvent freezes appreciably above the freezing-point of water, it is only necessary to use water and ice. If we are working with water as the solvent, the freezing-mixture more commonly used is ice and salt. Care must be taken that not too much salt is used, since, when the mixture is too cold, the results obtained are often not reliable.

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[1] *Ztschr. phys. Chem.* **1**, 633 (1887).
[2] *Ibid.* **2**, 638 (1888).
[3] *Ibid.* **2**, 306 (1888).

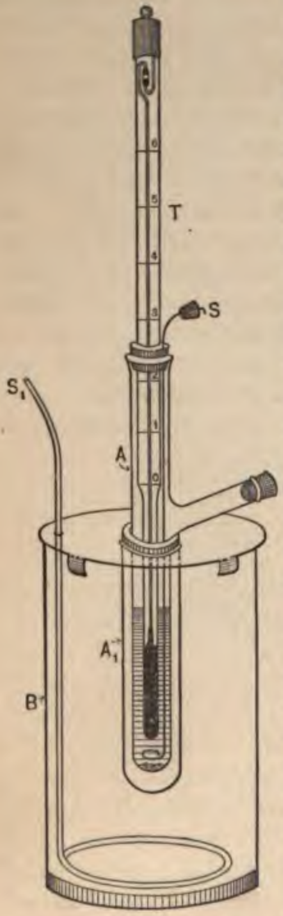

FIG. 24.

The thermometer used by Beckmann requires special comment. It is constructed on a different plan from that of any other thermometer which has ever been used. In the first place, the bulb is very large, and, consequently, the divisions on the scale correspond to a very small range in temperature. The largest scale divisions correspond to degrees. The total range of such a thermometer is usually about 6°. The next smaller divisions correspond to tenths of a degree, and the smallest divisions to hundredths of a degree. By means of a small lens it is possible to read the scale to thousandths of a degree.

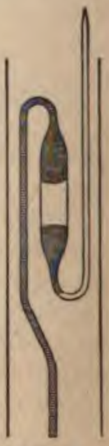

FIG. 25.

The unique feature of the Beckmann thermometer is, however, the arrangement at the top. This is seen in Fig. 25.

The capillary terminates in a reservoir or cistern, into which, by warming the bulb, mercury can be driven. The mercury in this reservoir can be thrown either to the top or bottom by holding the thermometer and tapping or thrusting it. By this means it is possible to increase or decrease the amount of mercury in the bulb of the thermometer, and to so adjust the amount that the top of the column will come to rest at any desired point on the scale, when the instrument is placed in the freezing solvent. The freezing-point of any solvent or solution can, then, be adjusted at any desired position on the scale, and the difference between the freezing-points of the solvent and solution determined. This differential thermometer of Beckmann has proved of incalculable service to physical chemistry, and has contributed more to our knowledge, in the field which we are now studying, than any invention or device which has ever been proposed. The Beckmann thermometer plays a rôle in physical chemistry which may be compared with that of the potash bulbs of Liebig in organic chemistry.

Method employed by Beckmann. — The method of working with the Beckmann apparatus is very simple. If we are dealing with aqueous solutions, enough water is introduced into the vessel *A* to cover the bulb of the thermometer. The freezing-point of the water is determined on the scale of the thermometer, and then redetermined. The two readings should not differ more than a very few thousandths of a degree. When the water is being cooled down in the vessel, it does not freeze as quickly as it reaches the zero point, but undercools, sometimes as much as two or three degrees, before the ice begins to separate. Ice will then separate until heat enough is liberated to warm the remaining water up to the freezing temperature. After the freezing-point of the water has been accurately determined on the thermometer, — and this must always be done just before the freezing-point of the solution is determined, — we then proceed to determine the freezing-point of the solution. The solution can be prepared in either of two ways. The water in the freezing-vessel can be weighed and then a weighed amount of the substance introduced; or the solution can be prepared in a measuring flask, using some of the same water whose freezing-point has just been determined. The method chosen for preparing the solution depends upon the amount of substance available, the solubility of the substance, concentration of solution desired, etc.

Having prepared the solution, its freezing-point must now be determined. We proceed in exactly the same manner in determining the freezing-point of a solution, as in the case of a pure solvent.

Duplicate determinations should differ only slightly from each other. The difference between the freezing-point of the solvent and that of the solution is the lowering of the freezing-point of the former produced by the dissolved substance.

The Separation of Ice concentrates the Solution. — When a pure solvent freezes, enough solid separates to warm the remaining liquid up to its freezing-point. The amount of solid formed depends, evidently, upon the amount of the undercooling and the heat of solidification of the solvent, which is obviously equal to its heat of fusion. In the case of a pure solvent there is no correction to be introduced for the separation of the solid phase, since the remainder of the liquid is unchanged.

When a solution freezes, the case is quite different. The pure solid separates from a solution as from the solvent alone. Since none of the dissolved substance separates, the solution becomes more concentrated, due to the freezing out of some of the solvent. Since the solution whose freezing-point is determined is more concentrated than that with which we started, some correction must be introduced for this increase in the concentration. The correction can be calculated very simply, as Jones[1] has pointed out. Let u be the undercooling of the solution in degrees, s the specific heat of the liquid, and l the latent heat of fusion of unit weight of the solvent, $\frac{su}{l}=f$, where f is the amount by which the solution will be concentrated, due to the separation of ice.

Determination of Molecular Weights by the Freezing-point Method. — One of the most important applications of the freezing-point method is the determination of the molecular weights of substances in solution in different solvents. A great number of such determinations have been made, and much light thrown on the nature of dissolved substances in general. The method used is generally that described by Beckmann and which has just been considered. Knowing the weight of the solvent, the weight of the dissolved substance, the lowering of the freezing-point produced, and the freezing-point constant of the solvent, it is quite simple to calculate the molecular weight of the dissolved substance. If M is the unknown molecular weight, W the weight of the solvent, w that of the substance, Δ the lowering of the freezing-point observed, and C the constant for the solvent, we have —

$$M=\frac{Cw}{\Delta W}.$$

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[1] *Ztschr. phys. Chem.* **12**, 624 (1893).

A word in reference to the freezing-point constant of a solvent. When a gram-molecular weight of a completely undissociated substance is dissolved in 1000 grams of water, the freezing-point of the water is lowered 1°.86. This value is known as the molecular lowering of water. When the molecular lowering is multiplied by 10, we have the values of the freezing-point constant given below for a few of the more common solvents: —

	C		C
Acetic acid	39.0	Formic acid	27.7
Benzene	50.0	Nitrobenzene	70.7
Ethylene bromide	117.9	Water	18.6

For details in connection with the application of the freezing-point method to the problem of molecular weight determinations, and for some of the results which have been obtained, hardly more than reference can be made to other works[1] which deal especially with these phases of our subject. It should, however, be stated here, that the molecular weights of non-electrolytes in water usually come out the simplest possible, showing that there is no aggregation of the molecules in such solutions. Such molecular weights correspond to those found in the state of vapor, by the vapor-density methods. It must not be concluded that the molecular weights in aqueous solutions are always the same as in the state of vapor, nor that the molecular weights in solution in water are always the simplest possible, since there are many exceptions to both of these conclusions. Other common solvents which do not favor the formation of molecular complexes are formic and acetic acids, phenol, aniline, etc.; while association frequently takes place in benzene, nitrobenzene, ethylene bromide, and the like.

Erroneous Conclusion from Freezing-point Determinations. — One error has so often arisen in connection with the determination of molecular weights in solution, that attention must be called to it in this connection. The freezing-point method gives us, as we believe, the molecular weight of the substance in solution, and in solution in the particular solvent in question. From such results conclusions are often drawn as to the molecular weight of the pure, homogeneous substance. Indeed, attempts have been made to show that certain isomeric and polymeric substances have the same molecular weights, because, when dissolved in some solvent, they show the same molecular weight.

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[1] A small laboratory guide on *Freezing-point, Boiling-point, and Conductivity Methods* has been prepared by H. C. Jones. A much more elaborate work is that of H. Biltz translated by Jones and King: *Practical Methods for Determining Molecular Weights* (Chem. Pub. Co.). See also Traube's *Physikalisch-chemische Methoden.*

This is, of course, all entirely unjustified. We do not know the connection between the molecular weight of a substance in solution and its molecular weight in the pure state, and until such a relation has been discovered, we must always bear in mind that the freezing-point method gives us only the molecular weight of the substance in the presence of the solvent with which we are working.

Dissociation as measured by the Freezing-point Method. — The second important application of the freezing-point method to physical chemical problems will now be taken up. The lowering of the freezing-point of water produced by electrolytes is always greater than that produced by non-electrolytes of the same gram-molecular concentration. This is explained, as we have seen, by assuming that a larger or smaller part of the molecules are dissociated into ions, the number depending upon the concentration of the solution and the nature of the dissolved substance. It is obviously impossible to determine the molecular weights of such substances in solution, since the value found would, for any given substance, be dependent upon the concentration of the solution, and at all concentrations would be smaller than the smallest possible molecular weight of the substance in question.

To compounds which are dissociated in solution the freezing-point method is applied for the purpose of measuring the amount of the dissociation. This is made possible by the fact that an ion and a molecule lower the freezing-point to the same extent. If a molecule dissociates into two ions (and it can never dissociate into less than two), the freezing-point lowering will be double that produced by an undissociated substance; if into three ions, the lowering will be three times as great; and so on. The method of calculating dissociation is obvious from the above statements. If the molecular lowering is divided by the constant for the solvent, we obtain the coefficient i. The dissociation α for binary electrolytes is obtained from the expression, —

$$\alpha = i - 1.$$

If the electrolyte is ternary, the molecules breaking down into three ions each, we have —

$$\alpha = \frac{i-1}{2},$$

and the same principle holds for electrolytes which yield a larger number of ions. It is thus possible to determine the amount of the dissociation of any electrolyte in water, up to dilutions of say $\frac{1}{500}$ normal.

In order that such determinations may have any scientific value, they must be made with a very considerable degree of accuracy. The method devised by Beckmann for molecular weight determinations is far too crude for work of this kind. We shall examine some of the more refined methods for determining freezing-points.

More Accurate Methods of measuring Freezing-points. — A method which was apparently an improvement on that of Beckmann was devised in 1892 by Jones.[1] This work was undertaken at the suggestion of Ostwald, in whose laboratory it was carried out. At this time there were two general methods of measuring dissociation, which will be described in the proper places, and these two gave results which differed very considerably. The object was to find a third method of measuring dissociation, to see with which of the other two the results would agree, if with either. The vessel which was to contain the solution was enlarged so that it held a litre. The larger volume of the liquid would be less susceptible to changes in external temperature. The apparatus was constructed so as to secure as uniform cooling as possible, and a much more efficient stirrer was devised and used. The thermometer employed was of the Beckmann type, but was about ten times the size of the ordinary Beckmann instrument. The scale, which comprised only 0°.6, was divided directly into thousandths of a degree, so that with a lens it was possible to read the scale to ten-thousandths of a degree. With this apparatus Jones measured the dissociation of a number of acids, bases, and salts, in aqueous solutions ranging in concentration from 0.1 to 0.001 normal; and the results obtained agreed very satisfactorily with those of another method, which has since been shown to be the most reliable measure of electrolytic dissociation. The results obtained by the third method, which differed from those obtained by the other two, have been shown to contain an error, and when this was corrected the three sets of results agreed very satisfactorily.

A number of improvements in the freezing-point method have been suggested since the above method was proposed. Lewis[2] attempted to improve the stirring device and other minor features.

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[1] *Ztschr. phys. Chem.* **11**, 110, 529 (1893); **12**, 639 (1893).

[2] *Ibid.* **15**, 365 (1894).

Loomis[1] took special precautions not to keep the freezing-mixture too cold, to keep his thermometer at the same temperature day and night, and to stir at a uniform rate. He has carried out a number of investigations which represent a large amount of very careful work. Ponsot[2] has also done much work on the problem of freezing-point lowerings, but his results are so very peculiar that it is impossible to pass judgment upon them. Nernst and Abegg[3] have made very valuable contributions to our knowledge of freezing-point lowerings, calling attention especially to the necessity in many cases of keeping the temperature of the freezing-bath only a little below that of the freezing-point of the liquid. They also showed the necessity of correcting, in certain cases, for the heat liberated in stirring, for the rate of cooling, etc.

The most accurate work, however, which has ever been done on freezing-points of solvents and solutions seems to be the recent investigations of Raoult,[4] — the father of all cryoscopic work. This has proved to be his last important contribution to science, Raoult having just died in Grenoble, France, where all his earlier cryoscopic work was done. His last work was thus a beautiful investigation along the same lines which brought him into prominence many years ago. This investigation will stand as a crowning glory to a life devoted with unusual zeal to the cause of pure science.

Abnormal Freezing-point Lowerings produced by Some Electrolytes in Concentrated Solutions. — The results obtained for the dissociation of electrolytes in water show that the dissociation increases with the dilution, from the most concentrated solutions investigated up to a dilution of about $\frac{1}{1000}$ normal, where it becomes complete. We should expect from these results, and also from those obtained by other methods, that the dissociation would continue to decrease with increase in concentration, however far the concentration might be carried. Such has recently been shown not to be the case.

Jones and Ota,[5] in their work on the nature of solutions of double chlorides, obtained irregular results in concentrated solutions by the freezing-point method.

Jones and Knight,[6] in their work on double chlorides and bromides, found that the molecular lowering increased with the concentration from a certain point, and then increased again from this point with the dilution, as would be expected. The increase in the molecular lowering became very marked at great concentrations; indeed, so pronounced that the molecular lowering of a normal solution was as great as, or greater than, the theoretical molecular lowering when all the salt was completely dissociated.

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[1] *Wied. Ann.* **51**, 500; **57**, 495; **60**, 523 (1894–1897).

[2] *Ann. Chim. Phys.* [7], **10**, 79 (1897).

[3] *Ztschr. phys. Chem.* **15**, 681 (1894).

[4] *Ibid.* **27**, 617 (1898).

[5] *Amer. Chem. Journ.* **22**, 5 (1899).

[6] *Ibid.* **22**, 110 (1899).

This was evidently a remarkable and surprising fact, and obviously merited careful study. Jones and Chambers[1] took up the subject systematically, and determined the freezing-point lowerings produced by concentrated solutions of a number of chlorides and bromides. They used calcium, barium, strontium, magnesium, and cadmium chlorides and bromides. They found the increase in molecular lowering with increase in concentration from a certain point, for every salt except cadmium chloride and bromide. The results obtained with one chloride and bromide will bring out the point. Column I gives the concentration in terms of normal; column II, the corrected lowering of the freezing-point (corrected for separation of ice); column III, the molecular lowering.

CALCIUM CHLORIDE			CALCIUM BROMIDE		
I	II	III	I	II	III
0.102	0°.508	4.98	0.04355	0°.228	5.24
0.153	0°.752	4.91	0.08710	0°.445	5.11
0.204	1°.012	4.96	0.1306	0°.664	5.07
0.255	1°.267	4.97	0.1742	0°.904	5.18
0.306	1°.537	5.02	0.2613	1°.368	5.23
0.408	2°.104	5.16	0.3484	1°.847	5.30
0.510	2°.681	5.26	0.4355	2°.397	5.50
0.612	3°.348	5.47	0.5226	2°.949	5.64

It will be observed that there is a minimum in the molecular lowering of the freezing-point, from which this value increases both with dilution and with concentration. The existence of such a minimum is shown best by plotting the results in curves. The two sets of curves show the results which were obtained, the one with chlorides, the other with bromides. Cadmium chloride and bromide show no sign of a minimum in the molecular lowering. The results which were earlier obtained by Jones[2] for sodium chloride are given for the sake of comparison.

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[1] *Amer. Chem. Journ.* **23**, 89 (1900).

[2] *Ztschr. phys. Chem.* **11**, 529 (1893).

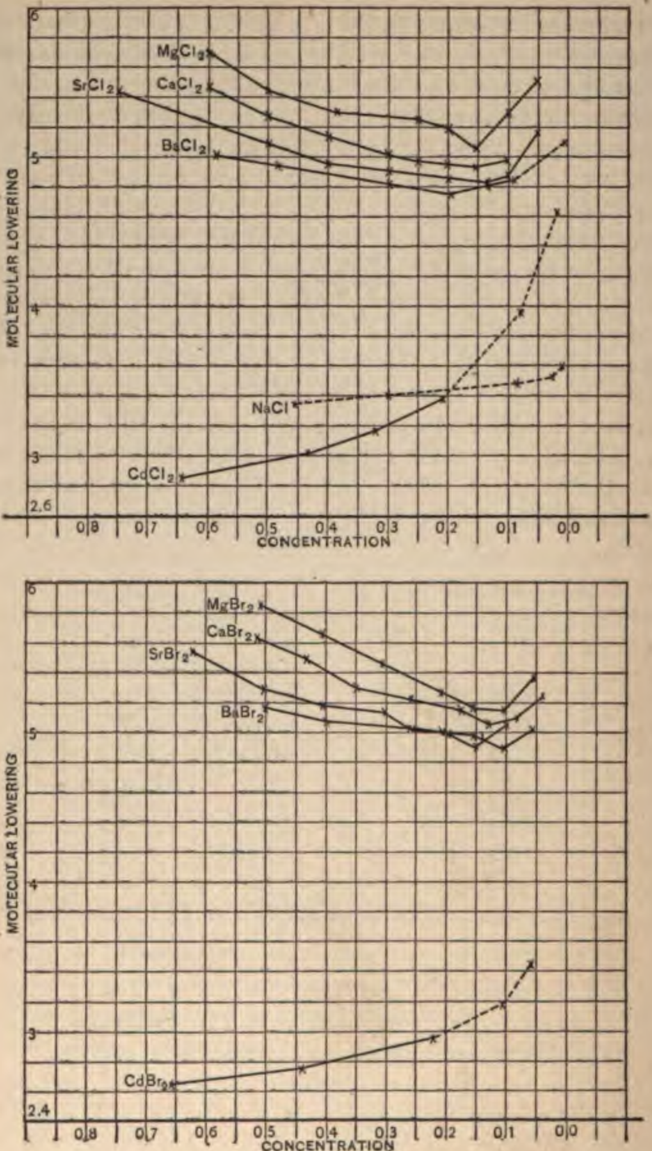

FIG. 26.

The work has since been extended by Chambers and Frazer.[1] They worked with hydrochloric and phosphoric acids, sodium acetate, copper sulphate, zinc chloride, and strontium and cadmium iodides. In every one of these cases they found a more or less pronounced minimum in the molecular lowering of the freezing-point.

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[1] *Amer. Chem. Journ.* **23**, 512 (1900).

Possible Explanation. — What is the explanation of the abnormal behavior of these substances? Jones and Chambers[1] have offered a tentative suggestion to account for these facts. It will be observed that nearly all of these substances are quite hygroscopic. Indeed, the work was directed toward the study of compounds which have this property. It seemed to them that the only explanation is that in concentrated solutions these substances take up a part of the water, forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The unstable compound formed by the union of one molecule of the substance with a large number of molecules of water, acts as one molecule in lowering the freezing-point of the remaining water. But the total water present, which is then acting as solvent, is diminished by the amount taken up by the substance. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the molecules of the dissolved substance. By assuming, then, that a molecule of the dissolved substance is in combination with a large number of molecules of water, it is possible to explain all of these apparently abnormal results.

Evidence in Favor of the Above Explanation. — It is not a simple matter to obtain direct evidence bearing on this point. A bit of indirect evidence has, however, been furnished by working with another substance. It was vigorously maintained, especially by Mendeléeff, that sulphuric acid forms compounds with water in dilute solutions. These compounds were represented as very complex, containing one molecule of sulphuric acid and a large number of molecules of water. If this was true, it was at variance with the theory of electrolytic dissociation, since this theory claimed not only that there were no such compounds in dilute solutions, but that the dissolved substance itself actually broke down or dissociated into ions.

An investigation to test the correctness of Mendeléeff's conclusion was carried out in the laboratory of Arrhenius in 1893, by Jones.[2] The lowering of the freezing-point of dry acetic acid by water alone was determined; then, the lowering of the freezing-point of acetic acid by sulphuric acid; and, finally, the lowering of the freezing-point of acetic acid by water and sulphuric acid together. The result was to show that there is not the slightest evidence in favor of Mendeléeff's theory of the existence of very complex hydrates in dilute solutions. But it also showed that there are undoubtedly compounds formed in solution between the acid and water, having the composition $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 2\,H_2O$. When the amount of water present was about thirty times that of the sulphuric acid, no compounds having greater complexity were formed, as was shown by the freezing-point lowering of the acetic acid.

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[1] *Amer. Chem. Journ.* **23**, 103 (1900).

[2] *Ztschr. phys. Chem.* **13**, 419 (1894); *Amer. Chem. Journ.* **16**, 1 (1894).

If sulphuric acid can combine with water in concentrated solutions, forming compounds like the above, why may not other hygroscopic substances have the same power? This line of evidence is, of course, no proof of our theory, but it shows that there are analogous cases known, and has the same weight as other lines of reasoning based upon analogy.

Whatever the explanation may be, the facts have been established beyond question, and we now know that molecular lowering of the freezing-point does not always increase with the dilution, but may also, in some cases, increase with the concentration.

Freezing-points of Amalgams. — The lowering of the freezing-point of mercury, produced by dissolved metals, has been studied by Tammann.[1] The value of the constant for mercury, as calculated by a method which will soon be discussed, was found to be 425. Tammann worked with solutions of potassium, sodium, thallium, zinc, and bismuth, in mercury, and determined the molecular weights of the dissolved metals. The molecular weights calculated from his results are as follows: —

	MOLECULAR WEIGHTS	ATOMIC WEIGHTS
Potassium	26–55	39
Sodium	21–25	23
Thallium	141–221	200
Zinc	52–66	65

These results show that the molecular weights of metals dissolved in mercury are practically identical with their atomic weights. The molecule of the metals in such solutions contains one atom.

Tammann also extended his work to solutions of metals in sodium, and studied the freezing-points of such alloys. Solutions of metals in sodium have also been investigated by Heycock and Neville.[1] They found that the law of Raoult applies to such solutions. One atom of a metal, dissolved in one hundred atoms of sodium, produced a constant lowering of the freezing-point, almost regardless of the nature of the dissolved metal. Similar results were obtained with tin as a solvent. The law of Raoult applied here, the atomic lowering being a constant except in a few cases as with aluminium, where the atomic lowering is much smaller than with other metals.

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[1] *Ztschr. phys. Chem.* **3**, 441 (1889).

Eutectic Alloys. — If we melt together any two metals which can dissolve one another, and allow the mixture to cool, we have an alloy. The freezing-points of such alloys are usually lower than those of the constituents, and a number of cases are known where the alloy freezes much lower than the lowest freezing constituent (*e.g.* Wood's metal, Rose's metal, etc.). The freezing-point of an alloy of any two metals depends upon the composition, *i.e.* the amount of each metal present. One particular alloy has some special interest, and has been given a definite name, which will be frequently encountered. The lowest freezing alloy is known as the *eutectic alloy*, or is frequently referred to simply as the *eutectic*.

Cryohydrates. — When a dilute solution freezes, the pure solvent separates in solid form. If the solution is saturated at ordinary temperatures, when it is cooled down to the freezing-point it becomes supersaturated, and some of the dissolved substance must separate from the solution. If the solution is just saturated at the freezing-point, and all overcooling is prevented, the ice and dissolved substance will separate in the same proportion in which they are present in the solution. If we continue to freeze such a solution, the temperature will remain unchanged until the whole has solidified. The temperature will also remain unchanged until the whole is melted again.

Guthrie[2] studied such substances, and termed them cryohydrates. He supposed them to be definite chemical compounds, since they had a constant melting-point and constant composition. This has been shown by Offer[3] not to be the case, since the heat of solution of a cryohydrate is equal to the sum of the heats of solution of the solid solvent and the dissolved substance. Further, the specific gravity of a cryohydrate is the same as that calculated by the law of mixtures from the specific gravities of the constituents. Since there is neither heat change nor volume change in the formation of cryohydrates, these cannot be regarded as chemical compounds.

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[1] *Journ. Chem. Soc.* **55**, 666 (1889); **57**, 376 (1890).

[2] *Phil. Mag.* [4], **49**, 1 (1875); [5], **1**, 49, and **2**, 211 (1876).

[3] *Bericht Wien. Akad.* **81**, II, 1058 (1880).

It will be seen at once that we have in these cryohydrates an admirable means of maintaining a constant, low temperature. It is only necessary to have some of the liquid cryohydrate in the presence of the solid to secure uniform temperature.

It is obvious that there is an analogy between a cryohydrate and a eutectic alloy. A eutectic is the lowest freezing-mixture of two metals; a cryohydrate is the lowest freezing-mixture of two substances.

Relation between Freezing-point Lowering and Osmotic Pressure. — A very close relation has been established between the power of the dissolved substance to exert osmotic pressure and to lower the freezing-point of the solvent. That such a relation exists has been shown both experimentally and theoretically.

De Vries, as we have seen, measured the relative osmotic pressures of solutions of different substances, and determined the concentrations which were isosmotic. If these concentrations are expressed in molecular quantities, their reciprocal values are known as isotonic coefficients, as has already been stated. These coefficients for a number of substances, as compared with the molecular lowerings of the freezing-point, are given in the following table, which is taken from the work of De Vries:[1] —

SUBSTANCE	ISOTONIC COEFFICIENTS MULTIPLIED BY 100	MOLECULAR LOWERING OF FREEZING-POINT MULTIPLIED BY 100
$C_6H_{12}O_6$	181	185
$C_{12}H_{22}O_{11}$	188	193
$MgSO_4$	196	192
KNO_3	300	308
$NaCl$	305	351
K_2SO_4	391	390
$CaCl_2$	433	466

The agreement between the two sets of values is as close as could be expected, when we consider that these results were obtained at different temperatures and concentrations. There is, then, undoubtedly a proportionality between osmotic pressure and lowering of freezing-point, so that *solutions of equal osmotic pressure have also the same freezing-point.*

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[1] *Ztschr. phys. Chem.* **2**, 427 (1888).

Demonstration of the Relation between Lowering of Freezing-point and Osmotic Pressure. — The relation between osmotic pressure and lowering of freezing-point was first deduced, thermodynamically, by Van't Hoff,[1] in his epoch-making paper to which reference has been made repeatedly. He showed that solutions in the same solvent, having the same freezing-point, are isotonic. Applying this to dilute solutions, he was led to the conclusion that solutions which contain the same number of molecules in the same volume, and, therefore, from Avogadro's law are isotonic, have also the same freezing-point. This was discovered experimentally by Raoult, and led to the expression, "normal molecular lowering of the freezing-point." This means the lowering in degrees, produced by a gram-molecular weight of the substance in 100 (or 1000) grams of the solvent. The normal molecular lowering of the freezing-point, which we will term the freezing-point constant for the solvent, Van't Hoff then derived from the latent heat of fusion of the solvent.

This deduction has been worked out more fully by Ostwald,[2] and it will be given here essentially in the form proposed by him, with some modifications[3] which seem to make the several steps a little clearer.

The solution with which we shall deal contains n molecules of substances dissolved in N molecules of solvent, the lowering of the freezing-point being Δ. If M is the molecular weight of the dissolved substance, S the specific lowering of the freezing-point, and C the freezing-point constant, the formula of Raoult is —

$$M = \frac{C}{S}.$$

The specific lowering, however, is equal to the observed lowering Δ, divided by the percentage concentration p; $S = \frac{\Delta}{p}$.

Therefore,

$$M = \frac{Cp}{\Delta}.$$

But $n = \frac{p}{M}$, and substituting $p = nM$ in the last equation, it becomes

$$M\Delta = CMn,$$

or,

$$\Delta = Cn. \qquad (1)$$

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[1] *Ztschr. phys. Chem.* **1**, 481 (1887). Scientific Memoirs Series, IV, 29.

[2] *Lehrb. d. Allg. Chem.* **1**, 759.

[3] Jones: *Phil. Mag.* **36**, 493 (1893).

The solvent freezes at the temperature T, and we allow as much of the solvent to solidify as would contain one molecule of the dissolved substance, *i.e.* $\frac{N}{n}$ molecules.

If the latent heat of fusion of the solvent is λ, the heat set free in this process would be $\frac{N}{n}\lambda$.

The ice which has separated is fused by warming to the temperature T, and the liquid allowed to mix with the solution by passing through a semi-permeable membrane. An osmotic pressure will be exerted, which we will call p. If the volume of the solution is v, the work done is pv.

Since the heat liberated is $\frac{N}{n}\lambda$, we have —

$$pv : \frac{N}{n}\lambda = \Delta : T,$$

or,

$$\frac{pvn}{N\lambda} = \frac{\Delta}{T}.$$

Since $pv = RT$, and $R = 2$ calories,

$$\Delta = \frac{n}{N}\frac{2T^2}{\lambda}.$$

Substituting $N = \frac{100}{M}$, where M is the molecular weight of the solvent, we have—

$$\Delta = \frac{nM}{100}\frac{2T^2}{\lambda}. \qquad (2)$$

From equations (1) and (2),

$$C = \frac{M}{100}\frac{2T^2}{\lambda}.$$

Representing the heat of fusion of one gram of the solvent by L, we have $\lambda = LM$, and substituting this in the last equation, we have —

$$C = \frac{2T^2}{100\,L}.$$

The freezing-point constant of a solvent is thus calculated from the absolute temperature at which the solvent freezes, and the latent heat of fusion of the solvent.

From this equation Van't Hoff calculated the value of the freezing-point constant for a number of solvents, and compared the calculated values with those found experimentally.

SOLVENT	CONSTANT CALCULATED	CONSTANT FOUND
Water	18.7	18.6
Acetic acid	38.8	38.6
Formic acid	28.4	27.7
Nitrobenzene	69.5	70.7

It is obvious that the calculated[1] values agree satisfactorily with those found by experiment, and this confirms the conclusion reached experimentally, that osmotic pressure and freezing-point lowering are proportional.

Measurement of Osmotic Pressure by the Freezing-point Method. — We have seen that the direct measurement of osmotic pressure is an exceedingly difficult operation. Indeed, so difficult that it has been attempted by only a very few experimenters. After it was shown that there is direct proportionality between freezing-point lowering and osmotic pressure, the measurement of the latter became relatively a simple matter. It was only necessary to determine the freezing-point lowering produced by the dissolved substance, in order to calculate the osmotic pressure of the solution in question. A normal solution of a completely undissociated substance exerts an osmotic pressure of 22 atmospheres. Such a solution freezes 1°.86 lower than pure water. A lowering of the freezing-point of 1°.86 corresponds, then, to an osmotic pressure of 22 atmospheres. The osmotic pressure of any aqueous solution is obtained from the freezing-point lowering Δ, by multiplying by $\frac{22}{1^\circ.86}$

$$\text{Osmotic pressure in atmospheres} = \Delta \times \frac{22}{1^\circ.86}.$$

The freezing-point method, on account of the ease with which it can be carried out, furnishes the best means of measuring the osmotic pressure of solutions in solvents which freeze near the ordinary temperature.

The freezing-point method has, indeed, three distinct applications: The determination of the molecular weights of non-electrolytes in solution; the measurement of the electrolytic dissociation of electrolytes; and the measurement of the osmotic pressure of both electrolytes and non-electrolytes. Each of these applications has been discussed at sufficient length, and we now pass to another property of solutions.

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[1] The constants for a large number of solvents are given by Biltz, in *Practical Methods for Determining Molecular Weights*, p. 106. From these the latent heats of fusion are calculated by the Van't Hoff equation.

LOWERING OF THE VAPOR-TENSION OF SOLVENTS BY DISSOLVED SUBSTANCES (RISE IN BOILING-POINT)

Earlier Work. — Every solvent has, under a given pressure, a definite temperature at which it freezes. So, also, every solvent, at a given temperature, has a definite vapor-pressure. We have seen that the presence of a foreign substance in solution lowers the freezing-point. We shall now learn that the presence of a dissolved substance lowers the vapor-tension of the solvent, unless the dissolved substance has itself, under the conditions, an appreciable vapor-tension.

The mere qualitative fact was early observed, and quantitative measurements were made early in the century by Faraday and others. The first to arrive at any generalization of importance in this field was Wüllner.[1] He studied especially aqueous solutions of salts, and compared directly the vapor-tensions of the solutions with those of pure water at the same temperature. He found that the *lowering of the vapor-tension of water by non-volatile, dissolved substances is proportional to the amount of substance present.* This is evidently analogous to the law of Blagden for freezing-point lowering, and, as we shall see, like the latter is only an approximation which holds in certain cases.

About a quarter of a century later Tammann[2] studied more carefully the vapor-pressure of aqueous solutions of salts. He found that the molecular lowerings of the vapor-pressure, produced by salts which were of similar composition, were very nearly the same. He also pointed out that the law of Wüllner is only an approximation, the depression of the vapor-tension increasing in some cases more rapidly, in others less rapidly than the concentration.

The experiments of Emden[3] were made with the best apparatus which had been used up to that time. He confirmed a relation which had been early pointed out by Von Babo, that the relation between the vapor-pressure of the solution and the solvent is independent of the temperature, at least from 20° to 95°.

While the work of Walker[4] really belongs to a later period than that of Raoult, which will be taken up next, it seems best to deal with it in this connection. Walker measured the vapor-pressure of salt solutions at low temperatures, using a very simple apparatus. It consisted of three Liebig bulbs and a U-tube. Bulbs 1 and 2 contained the solution to be investigated, bulb 3 distilled water, and the U-tube pumice moistened with sulphuric acid. The whole was kept at a constant temperature. A slow current of air, dried over sulphuric acid, was drawn through the entire system. The air, in passing through the solution, took up an amount of water corresponding to the vapor-pressure of the solution. The second tube containing the solution lost but little water, and, therefore, this solution underwent no appreciable change in concentration. The air passed from the solution into the pure water, and here took up more water, since the vapor-tension of the solvent was greater than that of the solution. The air, now saturated at the temperature of the experiment, was then passed over the sulphuric acid, to which it gave up practically all the water which it had taken both from the solution and the solvent. Walker states[1] that the average time of an experiment was twenty-two hours. After the experiment was ended each tube was weighed, and it was thus determined how much water was taken up from the solutions and how much from the pure solvent. The ratio of the loss in weight of the pure solvent, to the gain in weight of the tube containing sulphuric acid, gives the relative lowering of the vapor-pressure. The method is obviously very simple and can be rapidly carried out. By means of it we can easily study the vapor-pressures of dilute solutions at low temperatures. The results obtained agree closely with those of Emden.

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[1] *Pogg. Ann.* **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[2] *Wied. Ann.* **24**, 523 (1885).

[3] *Ibid.* **31**, 145 (1887).

[4] *Ztschr. phys. Chem.* **2**, 602 (1888).

The Work of Raoult. — We have seen that the work of Raoult marked a new epoch in cryoscopic investigations. We shall now see that his work on vapor-tension threw new light on this entire field, and is by far the most important which has ever been done on this subject.

The earlier investigators had chiefly used water as the solvent, and electrolytes (especially salts) as the dissolved substances. We have seen that this is just the solvent which produces electrolytic dissociation, and the electrolytes the dissolved substances which undergo dissociation. And the amount of the dissociation depends upon the dilution of the solution. Under such condition it was, then, almost hopeless to try to discover relations or to arrive at any wide-reaching generalization.

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[1] *Ztschr. phys. Chem.* **2**, 603 (1888).

Raoult[1] used a solvent which has but little dissociating power, and which has a high vapor-tension at ordinary temperatures. He worked with solutions in ether. The substances which were dissolved in the ether were organic compounds, which would not be dissociated by even the strongest dissociating solvent, and still less by ether.

Raoult used glass tubes of 1 cm. internal diameter, in which to measure the vapor-pressure of solvent and solution, and took great precautions in reference to keeping the whole at a known, constant temperature. Corrections were introduced for the increase in the concentration of the solution due to the formation of vapor, for capillarity, etc.

He did most of his work at ordinary temperatures, but studied the *effect of temperature* on the vapor-pressure of ethereal solutions. This work covered the range from 0° to 22°, and within this range the relative vapor-pressures of solution and solvent were constant. This is shown by the following results, t is temperature, f is the vapor-pressure of pure ether, and f' the vapor-pressure of the solution.

16.482 GRAMS OF OIL OF TURPENTINE IN 100 GRAMS OF ETHER

t	f	f'	$\frac{f'}{f} \times 100$
1°.1	199.0	188.1	91.5
3°.6	224.0	204.7	91.4
18°.2	403.5	368.7	91.0
21°.8	472.3	430.7	91.2

10.442 GRAMS OF ANILINE IN 100 GRAMS OF ETHER

t	f	f	$\frac{f'}{f} \times 100$
1°.1	199.5	183.3	91.9
3°.6	223.2	204.5	91.6
9°.9	289.1	264.0	91.3
21°.8	472.9	432.7	91.5

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[1] *Ann. Chim. Phys.* [6], **15**, 375 (1888). *Ztschr. phys. Chem.* **2**, 353 (1888). Scientific Memoirs Series, IV; English by H. C. Jones.

Between 0° and 22° the relative vapor-pressure is evidently independent of the temperature.

Raoult also studied the effect of *concentration of solution* on the vapor-pressure of ethereal solutions. He wished to use substances which are soluble in all proportions in ether, but all such have an appreciable vapor-tension. He chose those whose vapor-tension is lowest, such as oil of turpentine, aniline, nitrobenzene, ethyl salicylate, etc. These substances boil from 160° to 222°.

The results, extending over a fairly wide range of concentration, show that in general the relative lowering of the vapor-pressure is proportional to the concentration.

The most important point, however, which was tested by Raoult, was the *effect of the nature of the dissolved substance on the vapor-pressure of ethereal solutions, and, finally, on the vapor-pressure of solutions in different solvents.* We will take first solutions in ether as the solvent. A number of difficultly volatile substances were dissolved in ether, and the lowering of the vapor-tension measured. The relative lowering of the vapor-tension $\frac{f-f'}{f}$ was determined, and also the value of the quotient $\frac{f-f'}{fN}$, where N represents the number of molecules of the substance in 100 molecules of the solution.

			$\frac{f-f'}{fN}$
Hexachlorethane,	C_2Cl_6	$= 237$	0.0100
Nitrobenzene,	$C_6H_5NO_2$	$= 123$	0.0084
Ethyl benzoate,	$C_9H_{10}O_2$	$= 150$	0.0095
Benzoic acid,	$C_7H_6O_2$	$= 122$	0.0097
Trichloracetic acid,	$C_2Cl_3O_2H$	$= 163.5$	0.0105
Aniline,	C_6H_7N	$= 93$	0.0106
Antimony chloride,	$SbCl_3$	$= 228.3$	0.0087

The value of $\frac{f-f'}{fN}$ is evidently very nearly a constant, independent of the nature of the substance dissolved in the ether. The mean value for some fourteen substances is 0.0098, which is very close to 0.01.

The Law of Raoult. — Raoult employed different solvents,[1] and determined the lowering of their vapor-tension produced by dissolved substances. If we represent the molecular weight of the dissolved substance by M, the weight of substance in 100 grams of solvent by P, the molecular lowering, C, is expressed thus: —

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[1] *Compt. rend.* **104**, 1430 (1887).

$$C=\frac{f-f'}{fP}M.$$

Raoult used twelve volatile liquids as solvents, and dissolved in these a number of substances as slightly volatile as possible, such as cane sugar, glucose, urea, naphthalene, anthracene, ethyl benzoate, aniline, nitrobenzene, benzoic acid, etc. He found the following remarkable relation: "If[1] we divide the molecular lowering of vapor-pressure, C, in a given volatile liquid, by the molecular weight of the liquid, M', *the quotient*, $\frac{C}{M'}$, which represents the relative lowering of pressure produced by one molecule of non-volatile substance in one hundred molecules of solvent, *is a constant.*"

SOLVENT	M'	C	$\frac{C}{M'}$
Water	18	0.185	0.0102
Phosphorus trichloride	137.5	1.49	0.0108
Carbon bisulphide	76.0	0.80	0.0105
Tetrachlormethane	154.0	1.62	0.0105
Chloroform	119.5	1.30	0.0109
Amylene	70.0	0.74	0.0106
Benzene	78.0	0.83	0.0106
Methyl iodide	142.0	1.49	0.0105
Ethyl bromide	109.0	1.18	0.0109
Ether	74.0	0.71	0.0096
Acetone	58.0	0.59	0.0101
Methyl alcohol	32.0	0.33	0.0103

Although the values of M' and C vary as greatly as in the above table, the ratio, $\frac{C}{M'}$, is practically constant, and has the value 0.0105.

Raoult states his law as follows:[2] "*One molecule of a non-saline, non-volatile substance, dissolved in one hundred molecules of any volatile liquid, lowers the vapor-pressure of this liquid by a nearly constant fraction of its value — approximately 0.0105.*" This law, it will be recognized at once, is strictly analogous to that discovered by Raoult for the lowering of the freezing-point of solvents. It will be shown a little later that the two classes of phenomena are very closely connected.

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[1] Scientific Memoirs Series, IV, 127. Edited by Ames (Amer. Book Co.).

[2] *Ztschr. phys. Chem.* **2**, 372 (1888).

Determination of Molecular Weights from the Lowering of Vapor-tension. — The possibility of determining the molecular weights of dissolved substances by measuring the lowering of the vapor-tension of solvents produced by them, was clearly pointed out by Raoult.[1] The law of Raoult can be formulated thus: —

$$\frac{f-f'}{f}=C\frac{n}{N+n},$$

in which n is the number of molecules of the dissolved substance, N the number of molecules of the solvent, and C a constant. Since C is practically unity, the above expression becomes: —

$$\frac{f-f'}{f}=\frac{n}{N+n}.$$

If we represent the molecular weight of the substance by M, and the weight of substance used by w, $n=\frac{w}{M}$. Making $N=1$ and substituting this value of n in the above expression, we have —

$$\frac{f-f'}{f}=\frac{w}{M+w},$$

or,

$$M=\frac{wf'}{f-f'}.$$

Knowing w, f, and f', we can calculate M, the molecular weight of the substance in question. This method of determining molecular weights has never found extensive application in the laboratory, partly on account of the comparative difficulty involved in measuring vapor-pressure, and chiefly because it was quickly supplanted by a method which can be carried out far more accurately and rapidly in practice. Furthermore, certain serious sources of error in the measurement of vapor-tension have been pointed out by Tammann.[2] If there is present as an impurity in the solvent any more volatile substance, it will affect the vapor-pressure very considerably. And, again, if the solution is not kept actively stirred, the layer at the surface will become more concentrated, due to the evaporation of the solvent from this portion of the solution. The vapor-tension will, then, be that of the more concentrated solution, and, consequently, lower than the true vapor-tension of the solution.

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[1] Scientific Memoirs Series, IV, 127. Edited by Ames (Amer. Book Co.).

[2] *Wied. Ann.* **32**, 683 (1887).

The Work of Beckmann. — Beckmann[1] began his work by improving the method for measuring vapor-tension, but soon abandoned the vapor-tension method altogether as a means of determining molecular weights. Instead of determining the relative vapor-tensions of solvent and solution at a given temperature, he determined the temperatures at which both solvent and solution have the same vapor-pressure. It was found to be especially convenient to determine the temperatures at which the vapor-pressures of the liquids are just equal to the pressure of the atmosphere. In a word, to determine the boiling-points of the pure solvent and of the solution, since the boiling-points are temperatures of equal vapor-pressure.

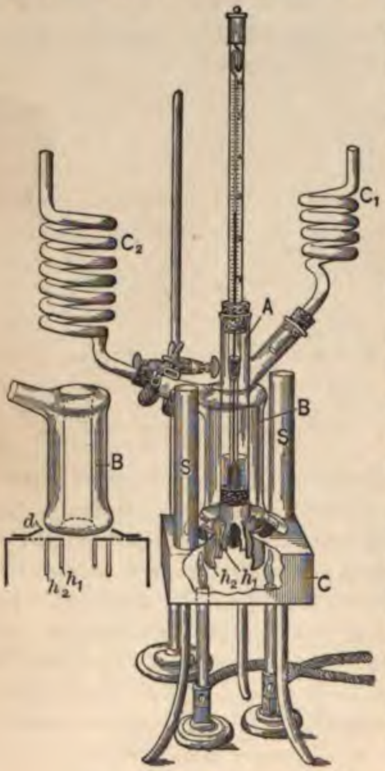

FIG. 27.

We have seen that the vapor-tension of a solvent is greater than that of a solution at the same temperature. The boiling-point of the solvent is, therefore, lower than that of the solution. The method as carried out by Beckmann consists in determining the *rise in the boiling-point of a solvent* produced by a dissolved, non-volatile substance.

The *apparatus* first devised[2] by Beckmann for determining the boiling-points of solvents and solutions has been so greatly improved that it is now of hardly more than historical interest. The best form[3] which has ever been suggested by Beckmann is shown in Fig. 27. The glass tube A contains the liquid whose boiling-point is to be determined. Into this liquid the thermometer dips, as shown in the figure. In the bottom of the tube are placed glass beads, garnets, or platinum scraps, so as to secure a more uniform rate of boiling. A condenser is attached to the tube *A*, as shown in the figure. This tube is surrounded by a double-walled glass jacket *B*, into which is introduced some of the same liquid whose boiling-point is to be determined in *A*. This is also provided with a return condenser. The liquid in *B* is boiled at the same time as the liquid in *A*, so that the innermost vessel is surrounded by a layer of liquid having the same boiling-point. The whole apparatus rests upon an asbestos box, and heat is supplied by a flame placed beneath. Beckmann has devised a number of modifications[1] of this apparatus, but in the opinion of the writer none of them represents any marked improvement on the form just described.

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[1] *Ztschr. phys. Chem.* **4**, 532 (1889).

[2] *Ibid.* **4**, 544 (1889).

[3] *Ibid.* **8**, 226 (1891).

Carrying out a Molecular Weight Determination with the Beckmann Apparatus. — The pure solvent is poured into the tube *A*, the filling-material (beads or garnets) introduced, and the thermometer inserted so that when the cork is forced into the top of tube *A* the bulb of the thermometer is entirely covered by the liquid, but does not touch the glass beads. The mercury in the Beckmann thermometer is so adjusted that the top of the column comes to rest between the divisions 0° and 1° when the solvent boils. The vessel *A* is then carefully cleaned and dried, and after introducing the filling-material a weighed amount of the solvent is poured in. The thermometer is inserted and the condenser attached. Some of the pure solvent is poured into the vapor-jacket, and boiled simultaneously with that in the tube *A*. The position of the mercury is carefully noted on the thermometer, after the solvent has boiled about twenty minutes, and the barometer is also very carefully read. The flame is now removed and the solvent allowed to cool.

The substance whose molecular weight is to be determined is pressed into tablets, weighed, and introduced into the solvent. The boiling is renewed after all the substance has dissolved, and the temperature at which the solution boils carefully noted on the thermometer. The barometer is read again, and if any change has occurred, the proper correction[2] is introduced into the readings on the thermometer. Care must always be taken to tap the thermometer before making a reading. The difference between the boiling-point of the solvent and that of the solution is the rise in boiling-point produced by the dissolved substance.

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[1] *Ztschr. phys. Chem.* **15**, 656 (1894); **17**, 107 (1895); **18**, 492 (1895); **18**, 661 (1895); **21**, 245 (1896).

[2] For details see Biltz: *Practical Methods for Determining Molecular Weights*, translated by Jones and King; also Jones: *Freezing-point, Boiling-point, and Conductivity Methods* (Chem. Pub. Co.).

The calculation of the molecular weight of the dissolved substance from the rise in boiling-point is very simple. The rise in boiling-point is directly proportional to the lowering of the vapor-pressure, and, therefore, depends upon the relative number of molecules of the solvent and of the dissolved substance. If we represent the unknown molecular weight by m, the weight of the substance used by w, the weight of the solvent by W, and the rise in the boiling-point of the solvent by R, we have —

$$m = \frac{Cw}{RW}.$$

The value C is a constant for every solvent, and is the molecular rise in the boiling-point of the solvent produced by a completely undissociated substance. It can be either determined experimentally, or can be calculated by a method which will be described later. Molecular weights, as determined by the boiling-point method, usually are the simplest possible, though there are many exceptions to this generalization.

Improvements in the Boiling-point Apparatus of Beckmann. — A number of modifications of the Beckmann apparatus have been proposed, in addition to those suggested by Beckmann himself. Hite[1] introduced one glass tube into another, and placed the thermometer in the innermost tube, in order that the cold, recondensed solvent might not come in contact with the thermometer before it had been reheated. He also, by means of a glass cap into which notches had been filed, caused the steam to rise in very fine bubbles through the liquid just around the bulb of the thermometer. He thought that in this way he could secure a better stirring of the liquid just around the thermometer. The apparatus of Hite is undoubtedly an improvement on any which had been proposed up to that time. In an attempt to improve the Hite apparatus, Jones[2] devised and used the following form (Fig. 28). Into the glass tube A, some glass beads or garnets are introduced. To the side tube A, the condenser is attached. Into the beads a cylinder of platinum P is inserted by placing the finger upon the top of the cylinder and gently shaking the whole apparatus. The liquid whose boiling-point is to be determined is introduced into A until the bulb of the thermometer, placed as shown in the figure, is covered. The liquid must not come within a centimetre, or a centimetre and a half, of the top of the platinum cylinder. The tube *A* is surrounded by a thick jacket of asbestos *J*, and rests on an asbestos board in which a circular hole is cut, and over which a piece of wire gauze is laid. Heat is supplied by means of a very small flame *B*, placed beneath the apparatus and protected by a metallic screen as shown in the drawing.

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[1] *Amer. Chem. Journ.* **17**, 507 (1895).

[2] *Ibid.* **19**, 581 (1897).

The essential difference between this apparatus and other forms is the platinum cylinder which is introduced into the boiling liquid. The object of this cylinder is twofold. It prevents the cooled recondensed solvent from coming in contact with the thermometer before it is reheated to the boiling-point. It reduces the effect of radiation to a minimum. If the bulb of the thermometer is surrounded only by the boiling liquid, or even if a layer of asbestos is wrapped around the glass tube, heat will be radiated out from the hot bulb on to colder objects in the neighborhood. The temperature of the bulb will always tend to be a little lower than that of the boiling liquid in which it is immersed. By surrounding the bulb with a piece of metal as nearly as possible at the same temperature as the bulb itself, the effect of radiation is reduced to a minimum.

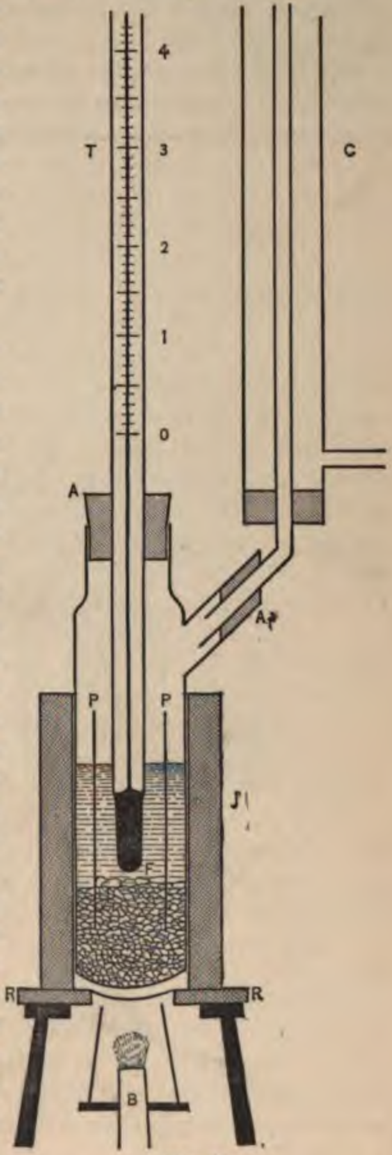

Fig. 28.

The apparatus is exceedingly simple, and when applied to the determination of molecular weights of dissolved substances, was found to give good results in both low-boiling and high-boiling solvents.[1] Another application of this method will be considered a little later.

The Apparatus of Landsberger as modified by Walker and Lumsden. — The apparatus of Landsberger[2] is based upon a somewhat different principle, especially with respect to the method of heating the liquid. The solvent or solution is heated to the boiling-point by means of the vapor of the pure solvent. The apparatus, as modified by Walker and Lumsden, is shown in Fig. 29.

A flask *F* contains the boiling solvent. The vapor is led through the tube *B* into the tube *N*, which contains the solution. This is surrounded by a larger tube *E*, which is connected with a condenser *C*. The vapor escapes from *N* through the hole *H*, and there is consequently a layer of vapor between *N* and *E*. The lower end of *R* contains a number of perforations through which the vapor escapes. The bulb *N* prevents the liquid from spattering through the opening *H*.

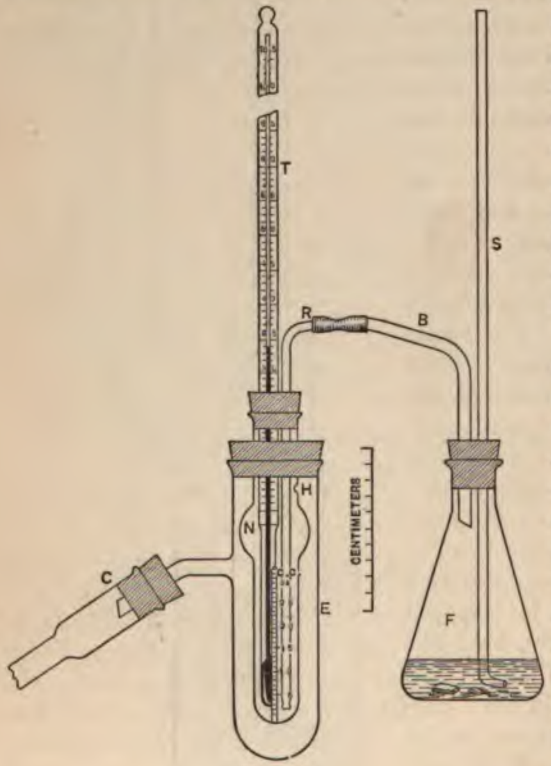

Fig. 29.

The pure solvent is poured into *N* until the bulb of the thermometer is just covered. The pure solvent in *F* is boiled after introducing some fragments of porcelain, and the vapor quickly boils the liquid around the thermometer. After this point is determined on the thermometer the tube is emptied, and a quantity of solution containing a known amount of dissolved substance in a given volume is added. The boiling-point of the solution is determined in the same manner as that of the solvent. The solution is continually changing concentration due to the condensation of vapor from the vessel *F*. After the boiling-point of the solution is determined, the inner tube, with thermometer and delivery tube, are weighed. Knowing the weight of this part of the apparatus empty, and the weight of the substance, we know the weight of the solvent.

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[1] *Amer. Chem. Journ.* **19**, 590 (1897).

[2] *Ber. d. chem. Gesell.* **31**, 458 (1893).

If a number of determinations are desired, using the same quantity of substance, the passage of the vapor is interrupted from time to time, the boiling temperature read, and the amount of solvent present determined. In such cases the volume of the solvent is read off, the tube *N* being graduated for this purpose. In reading the volume the thermometer and delivery tube are removed in each case from the solution. The object of heating the solution by means of its own vapor is to prevent any superheating, such as may take place when a flame is applied directly to the solution. The method as devised by Landsberger, and as modified by Walker and Lumsden, yielded good results in their hands when applied to the problem of molecular weight determinations.

Measurement of Dissociation by Means of the Boiling-point Method. — We have already seen how the freezing-point method can be applied to the measurement of electrolytic dissociation in solvents which freeze near the ordinary temperatures. There are, however, many of our most common solvents which do not freeze at temperatures to which that method is applicable, such as the alcohols, acetones, esters, etc. In many such cases we have absolutely no method for measuring the dissociation in these solvents, unless the boiling-point method could be applied. Jones and King[1] attempted to apply the boiling-point method to this problem, using the apparatus which had been designed by Jones. They measured the dissociation of one or two salts in ethyl alcohol, and showed that concordant results could be obtained.

The problem was subsequently studied far more extensively by Jones,[2] using his own apparatus. He used as solvents methyl and ethyl alcohols, and as dissolved substances, potassium, sodium, and ammonium bromides and iodides, potassium and sodium acetates, and calcium nitrate. The results obtained agreed satisfactorily with one another to within a per cent or two, and made it very probable that electrolytic dissociation could be measured by this boiling-point method to within a very few per cent.

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[1] *Amer. Chem. Journ.* **19**, 753 (1897).

[2] *Ztschr. phys. Chem.* **31**, 114 (1899) (Jubelband zu Van't Hoff).

The relative dissociating power of different solvents is, as we shall see, of more than the average interest, especially on account of certain theoretical questions which are involved. The dissociation of the above-named salts in water, and in ethyl and methyl alcohols, is given in the following table. The results with the alcohols are taken from the measurements of Jones, using the boiling-point method.

SUBSTANCE	DILUTION NORMAL	DISSOCIATION IN WATER	DISSOCIATION IN METHYL ALCOHOL	DISSOCIATION IN ETHYL ALCOHOL
KI	0.1	88 %	52 %	25 %
NaI	0.1	84	60	33
NH_4I	0.1	—	50	—
KBr	0.1	86	50	—
NaBr	0.1	86	60	24
NH_4Br	0.2	—	49	21
CH_3COOK	0.1	83	36	16
CH_3COONa	0.1	—	38	14
$Ca(NO_3)_2$	0.1	—	15	5

The interpolations by which the above values were obtained could be made only approximately, therefore the values of the dissociation are given only in whole numbers. It will be observed that the dissociation in methyl alcohol is more than half of that in water, while the dissociation in ethyl alcohol is less than one-third of that in water. Further relations between the dissociating power of different solvents will be discussed under electrochemistry.

The Vapor-pressure of Amalgams. — The molecular weights of metals dissolved in mercury were determined by the amount which they lowered the freezing-point of the mercury. Their molecular weights have also been determined from their depression of the vapor-tension of mercury. The following results are taken from the work of Ramsay:[1]—

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[1] *Journ. Chem. Soc.* **55**, 521 (1889).

METAL	MOLECULAR WEIGHT FOUND	ATOMIC WEIGHT
Lithium	7.10	7.02
Sodium	21.6–15.1	23.04
Calcium	19.1	40.1
Barium	75.7	137.0
Magnesium	24.0–21.5	24.3
Zinc	70.1–65.4	65.4
Gallium	69.7	69.9
Manganese	55.5	55.0
Silver	112.4	107.9

The molecular weights of most of the metals investigated by Ramsay, when dissolved in mercury, are the same as the atomic weights, showing that the molecule under these conditions consists of one atom. The cases of calcium and barium are exceptions; their molecular weights being one-half their atomic weights. This would show that what we are accustomed to call the atom of these elements is capable of subdivision, and is broken down in the presence of mercury into two parts.

The conclusion that the atom of calcium can be broken down was reached by Humphreys and Mohler,[1] from a study of the displacement of certain spectrum lines of calcium under pressure. They discovered a simple relation between the atomic volumes of the elements and the amount by which their lines are displaced when the vapor is subjected to pressure. In order that the relation should hold for calcium, it was necessary to assume that the atom had broken down into smaller parts. That two such independent lines of research should lead to the same general conclusion is certainly suggestive.

Relation between Lowering of Vapor-tension and Osmotic Pressure. — De Vries[2] has shown experimentally that a proportionality exists between the isotonic coefficients of a number of substances and the molecular lowering of vapor-tension. (Lowering of vapor-tension and rise in boiling-point are, of course, proportional.) The following results are taken from the work of De Vries:—

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[1] *Astro-Physical Journal*, **3**, 135 (1896).

[2] *Ztschr. phys. Chem.* **2**, 427 (1888).

Substance	Isotonic Coefficients multiplied by 100	Lowering of Vapor-tension multiplied by 1000
$C_4H_6O_5$	198	178
$C_6H_8O_7$	202	197
$NaNO_3$	300	296
$NaCl$	305	330
NH_4Cl	300	313
$K_2C_2O_4$	393	372
$K_2C_4H_4O_6$	399	388
$K_3C_6H_5O_7$	501	499

The proportionality between lowering of vapor-tension or rise in boiling-point and osmotic pressure, as established by experiment, is at once apparent.

Demonstration of the Relation between Lowering of Vapor-tension (Rise in Boiling-point) and Osmotic Pressure. — The relation between osmotic pressure and lowering of vapor-pressure has been derived in a simple manner by Arrhenius.[1] The line of reasoning is as follows: —

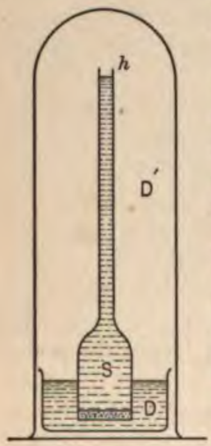

FIG. 30.

Given a vessel of the form shown in the figure, closed at the bottom by a semi-permeable wall. The vessel is filled with a solution *S*, and dips into another vessel containing the pure solvent *D*. The apparatus is covered with a bell-jar, and exhausted. Equilibrium will exist when the pressure of the column of liquid from the surface of the solvent up to *h*, is equal to the osmotic pressure. When equilibrium is established, the vapor-pressure of the solution at *h* must be just equal to the pressure of the vapor of the solvent at this point. If it were less, liquid would condense in *h*; if more, it would distil out of *h*, and there would not be equilibrium, since liquid would flow either out or in through the membrane. If f' is the tension of the vapor of the solution at *h*, f the vapor-tension of the solvent, *h* the height of the column of liquid, and *d* the density of the vapor, we have —

$$f' = f - hd.$$

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[1] *Ztschr. phys. Chem.* **3**, 115 (1889).

The Value of d. — Let v be the volume of a gram-molecule of the vapor of the solvent D, and f the pressure of this vapor: —

$$fv = RT,$$

$$v = \frac{RT}{f}.$$

If M is the molecular weight of the solvent, —

$$d = \frac{M}{v},$$

$$\frac{M}{d} = \frac{RT}{f}. \quad \therefore\ d = \frac{Mf}{RT}.$$

The Value of h. — Let us have a very dilute solution, in which n gram-molecules of substance are contained in g grams of solvent. From Van't Hoff's law of osmotic pressure we would have —

$$PV = RT \times n,$$

in which P is the osmotic pressure of the solution, and V its volume. Let s be the specific gravity of both solution and solvent (they are practically the same for very dilute solutions): —

$$P = h \times s;$$

$$V = \frac{g}{s}.$$

Substituting,

$$PV = nRT = \frac{hsg}{s} = hg;$$

$$hg = nRT. \quad \therefore\ h = \frac{nRT}{g}.$$

Substituting the values $h = \frac{nRT}{g}$ and $d = \frac{Mf}{RT}$ into the equation $f' = f - hd$, we have —

$$f' = f - \frac{nRT}{g} \times \frac{Mf}{RT}$$

$$= f - \frac{nMf}{g},$$

or,

$$\frac{f - f'}{f} = \frac{nM}{g},$$

which is essentially Raoult's fundamental equation for the lowering of the vapor-pressure of a solvent by a dissolved substance. Raoult's equation, which has been amply verified by experiment, is usually written —

$$\frac{f-f'}{f}=\frac{n}{N},$$

where N is the number of gram-molecules of the solvent. It is evident that $N=\frac{g}{M}$ when the two equations become identical.

Relation between Rise in Boiling-point and Lowering of Freezing-point. — Raoult has shown experimentally that the lowerings of the freezing-point produced by some eighteen salts stand in the same relation to one another as the rise in boiling-point produced by these same substances. The same relation has been repeatedly established by subsequent experiments.

That there is a relation between the two is demonstrated theoretically, by the fact that the formula which is used to calculate the freezing-point constant of a solvent can also be employed to calculate the boiling-point constant. The formula deduced (p. 224) for the freezing-point constant, $C=\frac{2\,T^2}{100\,L}$, gives us the boiling-point constant if we represent by T the absolute temperature at which the solvent boils, and by L the latent heat of vaporization of the solvent. The boiling-point constants for a few of the more common solvents are given below: —

Acetone	17.1	Aniline	32.0	Methyl alcohol	8.4
Ether	21.6	Benzene	26.1	Carbon bisulphide	23.5
Ethyl alcohol	11.7	Chloroform	35.9	Water	5.1
		Acetic acid	25.3		

The relations between osmotic pressure, freezing-point lowering, and rise in boiling-point have been then thoroughly established experimentally, and also demonstrated theoretically. The relation between each and the other two has been taken up and pointed out. Each of these properties depends only on the number of parts of the dissolved substance with respect to those of the solvent; it is a function of numbers. It does not matter whether the dissolved particle is a molecule or an ion, it has the same influence on all of these properties.

These three properties of solutions are among the most important from a physical chemical standpoint, and each has an interest peculiarly its own. But the fact that the three are so closely related increases our interest in each, and makes a study of them more important scientifically, since through such relations we arrive at wide-reaching generalizations — the highest aim of scientific investigation.

DIFFUSION

What is Diffusion? — When a solution of a colored compound, like copper sulphate, is placed in a glass cylinder and covered with water, the color is seen to rise gradually in the cylinder, and finally extends throughout its entire length. If the liquid is analyzed after a time, it will be found that the copper sulphate has passed into all parts of the cylinder. This is found to be a perfectly general property of dissolved substances. They always tend to distribute themselves throughout the entire solvent until all parts of the solution become homogeneous. This applies not simply to solutions bordering on the pure solvent, but also to one solution in contact with another. If the two solutions are of the same substance, the dissolved substance will always pass from the more concentrated to the more dilute solution, until homogeneity is established. If the two solutions are of different substances, each will distribute itself throughout the entire mass of the solvent present, until each has become perfectly homogeneous. This phenomenon is known as *diffusion*.

It is not easy to overestimate the importance of this property of dissolved substances, especially from the standpoint of the analytical chemist. If it was not for the power of dissolved substances to diffuse throughout the entire solvent present, it would be impossible to keep a solution homogeneous for any appreciable length of time. If the dissolved substance was heavier than the solvent, it would collect at the bottom of the solution; if lighter, it would collect at the top. In any case heterogeneity would result — the solution having different concentrations in different parts. Under such conditions standard solutions could not be preserved for any appreciable time. Since diffusion exists we can preserve a homogeneous solution for any length of time, provided only that we keep all parts at the same temperature. The importance of this property is at once evident; we shall now study it quantitatively.

Experiments of Graham. — The first experiments of any considerable importance on diffusion were those of Graham.[1] He did away with the use of any separating membrane, and used simply wide-mouthed vessels into which the solution was introduced. The vessel was then completely covered with water, allowed to stand, and the amount of substance which passed out by diffusion determined after a time. He found that the rates at which different substances diffuse varied greatly with the nature of the substance. Acids in general diffused more rapidly than salts, and the different salts varied greatly as to their diffusibility. Graham found that the constituents of some double salts, like the alums, could be partly separated by means of diffusion. He showed that the quantity of substance which diffuses in a given time is roughly proportional to the concentration of the solution originally employed.

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[1] *Phil. Trans.* 1850, 1, 805; 1851, 483. *Lieb. Ann.* **77**, 56, and 129 (1851); **80**, 197 (1851).

Fick's Law of Diffusion. — The first to arrive at any broad generalization in connection with the phenomenon of diffusion was Fick, and his law is probably the most important which has ever been discovered in connection with this phenomenon. Fick stated his law thus:[1] "*The amount of salt which diffuses through a given cross-section is proportional to the difference in concentration of two cross-sections lying infinitely near to one another, or is proportional to the difference in concentration.*"

Weber's Method of Measuring Diffusion. — After Fick had proposed his law a number of attempts were made to determine its accuracy. Weber[2] devised for this purpose a method which, for simplicity and accuracy, far exceeded all those which had been previously used. This method was based upon a principle which will be considered in detail under electrochemistry. A brief description of the principle must suffice in this place. If two plates of the same metal are immersed in solutions of a salt of that metal having different concentrations, and the plates connected, we have an element with a definite electromotive force. The electromotive force of such an element depends upon the difference in the concentration of the two solutions, and upon this fact is based the possibility of measuring diffusion by such a method.

A cylindrical vessel was closed at the bottom by an amalgamated plate of zinc. Upon this was poured a concentrated solution of a zinc salt. A more dilute solution of the same zinc salt was poured upon the more concentrated, and on the surface of the more dilute solution was placed a second plate of zinc. The two zinc plates were the electrodes, and the electromotive force of this couple at any instant depends upon the difference in concentration of the two solutions at that particular moment. The two solutions being placed in contact, diffusion of the zinc salt continually took place from the more concentrated to the more dilute solution. The difference in concentration became continually less, and, consequently, the electromotive force of the element became gradually smaller.

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[1] *Pogg. Ann.* **94**, 59 (1855).

[2] *Wied. Ann.* **7**, 469, and 536 (1879).

When the two solutions had, by diffusion, become of the same concentration, the electromotive force would of course entirely disappear.

Testing the Law of Fick. — If we apply Fick's law to this method, we obtain the following expression when the time is long: —

$$E = Ae^{-\frac{\pi^2}{H^2}kt}.$$

H is the height of the vessel used in the experiment, t is the time of the experiment, and A is a constant.

If the law of Fick is true, the expression $\frac{\pi^2}{H^2}k$ is a constant, independent of the time during which the experiment has lasted. Weber tested this point experimentally and obtained the following values: —

Days	$\frac{\pi^2}{H^2}k$
4– 5	0.2032
5– 6	0.2066
6– 7	0.2045
7– 8	0.2027
8– 9	0.2027
9–10	0.2049
10–11	0.2049

These results confirm at once the correctness of the law of Fick.

The law has been further tested by a number of different experimenters, using different methods. Scheffer[1] covered the solution with pure water, and determined the amount of substance which diffused upward into the water. He determined also the influence of concentration on the value of the diffusion constant k. The following results are taken from his paper, — n is the number of molecules of water to one molecule of substance, t is the temperature: —

	t	n	k
Sulphuric acid	11°.3	71.3	1.12
Sulphuric acid	7°.5	686.0	1.03
Nitric acid	9°.0	7.3	2.00
Nitric acid	9°.5	73.5	1.77
Nitric acid	9°.0	426.0	1.74
Hydrochloric acid	11°.5	7.5	2.74
Hydrochloric acid	11°.0	108.0	1.84
Ammonia	4°.5	15.9	1.06
Ammonia	4°.5	84.5	1.06
Sodium hydroxide	8°.0	329.0	1.05
Sodium hydroxide	8°.0	329.0	1.04
Calcium chloride	8°.5	19.1	0.70
Calcium chloride	10°.0	27.6	0.71

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[1] *Ber. d. chem. Gesell.* **15**, 788; **16**, 1903 (1882–1883). *Ztschr. phys. Chem.* **2**, 390 (1888).

With the exception of hydrochloric acid, the constant varies only slightly with the concentration, as would follow from the law of Fick.

Stefan[1] showed from the law of Fick as applied to a long vessel, that the quantity a, which diffused through a given area q, should be expressed thus:—

$$a = cq\sqrt{\frac{kt}{\pi}}.$$

This was tested experimentally by Voigtländer,[2] who worked with solutions in solid agar-agar jelly. It had already been shown by Graham,[3] and it was subsequently confirmed by Voigtländer, that the rate of diffusion was essentially the same in the jelly as in water. The advantages in using jelly instead of water in studying diffusion are obvious. The effect of jarring the solution would be lessened, and there would be far less mixing of the solution due to currents produced by unequal heating of different parts of the mass. By working with jelly solutions it was, then, possible to carry out diffusion experiments extending over a much greater period of time than had been practicable with aqueous solutions. Voigtländer[4] worked with a 0.72 per cent solution of sulphuric acid. He allowed this to diffuse into a cylinder containing agar-agar, and determined the amount a, which diffused through a square centimetre in a given time t. All the values of a were calculated on the basis of 60 minutes, hence the value 60 in the following constant.

TIME	AMOUNT DIFFUSED a	$a\frac{\sqrt{60}}{\sqrt{t}}$
5 minutes	0.30	1.04
40 minutes	0.86	1.05
120 minutes	1.48	1.05
300 minutes	2.44	1.09
900 minutes	4.30	1.11
1020 minutes	4.61	1.10
2880 minutes	7.05	1.02

These, and other similar results obtained by Voigtländer, agree with the formula deduced by Stefan, and confirm the law of Fick.

Voigtländer[5] also determined a number of diffusion constants of acids, bases, and salts; and the temperature coefficients between 0°–20°, and 20°–40°.

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[1] *Wien. Akad. Ber.* **79**, 161 (1879).

[2] *Ztschr. phys. Chem.* **3**, 316 (1889).

[3] *Phil. Trans.* 1861, p. 183.

[4] *Ztschr. phys. Chem.* **3**, 321 (1889).

[5] *Ibid.* **3**, 332 (1889).

The law of Fick has also been tested and confirmed repeatedly by subsequent work, so that it can now be regarded as a well-established law of nature.

The Cause of Diffusion. — What is the cause of diffusion? What force operates to drive the dissolved substance into all parts of the solvent until the whole becomes homogeneous? To obtain an answer to this question we must go back to the fundamental law of diffusion — the law of Fick. Diffusion depends upon difference in concentration, and upon this alone, temperature being constant.

This suggests at once the law of Boyle for the osmotic pressure of solutions. Osmotic pressure is proportional to concentration; *i.e.* it depends upon the difference in concentration of the solution and pure solvent, or of one solution and another. Since diffusion depends upon difference in concentration, and osmotic pressure depends upon difference in concentration, the question arises, is not osmotic pressure the cause of diffusion?

We shall see that this is very probably the case. In the first place, Boyle's law for osmotic pressure is strictly analogous to the law of Fick for diffusion. Again, the law of Gay-Lussac for osmotic pressure holds for the temperature coefficient of diffusion, as we have already seen. The principle of Soret is but an expression of this fact. It will be remembered that the change in concentration of a homogeneous solution, produced by keeping the different parts at different temperatures, is about $\frac{1}{273}$ of the original concentration for every difference of one degree in temperature. Here, then, we have two fundamental laws of osmotic pressure applying to diffusion.

Diffusion in solutions takes place very slowly, as we saw when discussing the principle of Soret, while diffusion in gases quickly establishes equilibrium. This is just what we should expect, even if osmotic pressure is exactly equal to gas-pressure under the same conditions. Equilibrium is established quickly in gases because there is comparatively little inner friction and the particles can move freely. The friction in solutions is much greater, due to the presence of the solvent, and, consequently, the dissolved particles move through the solvent much more slowly than the gas particles through space. Inner friction is, then, the chief cause for the long time required for diffusion to establish equilibrium.

To summarize, we can say that osmotic pressure and diffusion obey the same laws, and the former is either the cause of the latter, or they both have a common cause. Since we know of no such common cause we are justified in ascribing diffusion to osmotic pressure, and in regarding the latter as the cause of the former.

Nernst's Theory connecting Diffusion and Osmotic Pressure. — The relation between diffusion and osmotic pressure was brought out very clearly by Nernst[1] in his well-known paper on the "Theory of Diffusion." Van't Hoff had just shown the close analogy which exists between the osmotic pressure of dissolved substances and the gas-pressure of gases. Diffusion in gases was known to be due to the same cause as gas-pressure, *i.e.* in terms of the kinetic theory, to the movements of the gas particles; and the gas particles would move from a region of higher to that of lower pressure until equilibrium was established. Nernst saw clearly that there was a close analogy between diffusion in gases and diffusion of dissolved substances, the chief difference being in the time required to establish equilibrium. On the basis of these analogies Nernst made the following calculations, which will be given in his own words for non-electrolytes, since this is much simpler than for electrolytes: —

"Given, for the sake of simplicity, a diffusion cylinder of constant cross-section, and let us assume that the concentration in every cross-section is the same. If there is an osmotic pressure p at the place x, in the layer qdx there exists a pressure on the substance in solution of $-qdp$. If c is the concentration, *i.e.* the number of gram-molecules of the substance in question contained in a cubic centimetre, the force which at the place x acts on every gram-molecule is $-\frac{qdp}{qdxc}=-\frac{1}{c}\frac{dp}{dx}$. If we designate by K the force which must act on a gram-molecule in solution, in order to move it with the velocity of one centimetre per second, we have —

$$S=-\frac{qzdp}{Kdx},$$

the amount of substance in gram-molecules which wanders through the cross-section q in time z, if two layers about one centimetre apart show a difference of one in concentration. In the cases where the dissolved substance does not polymerize with increasing concentration, the osmotic pressure is proportional to the concentration, *i.e.*

$$p=p_0c,$$

where p_0 is the pressure in a solution of unit concentration, and we obtain —

$$S=-\frac{qzp_0}{K}\frac{dc}{dx}. \qquad (1)$$

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[1] *Ztschr. phys. Chem.* **2**, 613 (1888).

Since, however, in such great dilutions that the friction of the molecules of the dissolved substance against the molecules of the solvent is great with respect to their friction against one another, K is independent of the concentration; the elementary law of Fick for diffusion is at once derivable from the last expression. This law should hold rigidly for dilute solutions. At greater concentrations, on the other hand, deviations can arise, for the two following reasons: First, the force K can change with the concentration; second, the proportionality between p and c can cease to exist."

From the law of Fick the amount of salt S, which passes through the cross-section q of the diffusion cylinder in time z, if at x in the entire cross-section there is a concentration c (at $x + dx$ this is $c + dc$) is,

$$S = -k'qz\frac{dc}{dx}, \tag{2}$$

where k' is the diffusion coefficient for a given substance in a definite solvent.

From (1) and (2) we have: —

$$k' = \frac{p_0}{K}\ (\text{cm.}^2\ \text{sec.}^{-1}).$$

In calculating diffusion coefficients the units are the centimetre and day. If we designate this by k, we have —

$$k = \frac{p_0}{K}\, 8.64 + 10^4$$

(since there are $8.64 + 10^4$ seconds in a day).

The pressure p_0 is obtained from the volume occupied by a gram-molecular weight of a gas at 0°, and one atmosphere of pressure, *i.e.* the volume occupied by 2 grams of hydrogen or 32 grams of oxygen under a pressure of one atmosphere. According to the work of Regnault this volume is 22,380 cm. for hydrogen, and 22,320 cm. for oxygen. If we take the mean 22,350, we have the following: To compress a gram-molecular weight of a gas at $t°$ to a volume of one centimetre would require a pressure in atmospheres of —

$$22{,}350\ (1 + \alpha t) = p_0.$$

Since an atmosphere is equal to 1.033 kg.,

$$p_0 = 22{,}350 \times 1.033\ (1 + 0.0367\,t)$$

$$= 23{,}080\ (1 + 0.0367\,t)\ \frac{\text{kg.}}{\text{cm}^2}.$$

Substituting this value of p_0 in the above equation and solving for K, we have —

$$K = \frac{1}{k}\, 1.99 \times 10^9 \, (1 + 0.0367\, t) \text{ kg.}$$

To ascertain the absolute value of K for any given substance, it is necessary to know the value of the diffusion constant k. This has been determined for a number of substances by Scheffer.[1] From these determinations Nernst calculated the value of K for the following substances: —

	t	k	K
Urea	7°.5	0.81	2.5×10^9 kg.
Chloral hydrate .	9°.0	0.55	3.8×10^9 kg.
Mannite . . .	10°.0	0.38	5.5×10^9 kg.

From the calculations of k made by Stefan[2] on the basis of Graham's measurements, Nernst calculated the values of K for a number of substances.

	t	k	K
Caramel . . .	10°	0.047	44×10^9
Albumin . . .	13°	0.063	33×10^9
Cane sugar . .	9°	0.312	6.7×10^9

The enormous magnitude of these numbers is, of course, surprising. Thus, the force necessary to drive a gram-molecular weight of cane sugar through water with a velocity of one centimetre per second is 6700 million kilograms. Nernst raised the question as to whether this enormous resistance is closely connected with the weight, the constitution, and configuration of the molecules. Without attempting to answer it, he pointed out that the resistance undoubtedly increases with increase in molecular weight. This is clearly seen in the above table, where those substances which have the larger molecular weights have the larger values of K.

Ostwald[3] explains the enormous magnitudes of the above values as due to the very great number of molecules present in the solution

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[1] *Ztschr. phys. Chem.* **2**, 401 (1888).

[2] *Wiener Sitzungsberichte*, **79**, 161 (1879).

[3] *Lehrb. d. Allg. Chem.* I, p. 698.

— the molecular state representing matter in such a highly divided condition. As he states, the amount of force necessary to throw a stone through the air with a very considerable velocity is not great. If now the stone is powdered, the force required to project the dust with the same velocity is very great indeed. If then we consider this process of subdivision to continue until the molecules themselves are reached, the force required to hurl them through the air with the same velocity as was given the stone, would be enormous. If, finally, instead of through the air we hurl these infinitesimal particles through a highly resisting medium such as water, it is quite conceivable that the resistance encountered would be of the order of magnitude given above. Whether this is the expression of the whole truth, or not, it is certainly helpful in forming a conception of the possible cause of this very high resistance.

Nernst has also worked out a theory of diffusion for electrolytes,[1] but since this involves conceptions with which it would be premature to deal in this place, reference only can be made to it.

Crystalloids and Colloids. — The section on diffusion should not be closed without brief reference to a distinction between the velocities with which substances diffuse, which was pointed out by Graham.[2] If we compare the velocity with which an acid diffuses with that of albumin, we find that the two stand in the ratio of about 50 to 1. There are many substances which, like albumin, diffuse very slowly in the presence of water. These are chiefly amorphous substances, while those which diffuse rapidly are generally crystalline. The latter are termed *crystalloids*, the former *colloids*.

These two classes of substances, when in solution, affect the properties of the solvent very differently. Crystalloids, as we have seen, dissolve with temperature changes. They lower the freezing-point of the solvent, and also its vapor-tension. They exert an osmotic pressure. Colloids, on the other hand, affect the properties of the solvent to only a slight extent. If they lower the freezing-point or vapor-tension of the solvent, it is only to a very slight extent.

These two classes of substances can, in general, be easily separated from one another. If a solution containing both crystalloids and colloids is brought in contact with a colloidal membrane such as parchment paper, and water is placed on the other side of the membrane, the crystalloids will pass through the membrane, while the colloids will be prevented from doing so. This was termed by Graham *dialysis,* and the apparatus for effecting such separations a *dialyzer.*

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[1] *Ztschr. phys. Chem.* **2**, 617 (1888).

[2] *Lieb. Ann.* **121**, 1 (1862).

Colloidal Solutions of Metals. — Some unusually interesting results have recently been obtained in connection with colloidal solutions. It has been found possible to prepare colloidal solutions not only of the neutral, amorphous, organic substances, but of the metals themselves. A number of years ago Carey Lea[1] showed how metallic silver could be obtained in solution in water — the solution having the same properties as that of a colloid; and quite recently Bredig and Von Berneck[2] have worked up a more or less general method[3] for obtaining the most insoluble metals in the form of colloidal solutions. The method will be described as applied in the case of metallic platinum. Two platinum wires (*a* and *b*, Fig. 31), of about one millimetre diameter, are dipped into pure water and brought close together. A current of from 8–12 ampères and 30–40 volts is passed through the wires. This forms an electric arc under the water. The metal is torn off from the cathode in a very fine state of division, and the water quickly becomes dark brown in color. After the solution has acquired the concentration desired it is filtered through a folded filter to remove any larger particles of platinum which may have been torn off. When a drop of this liquid is placed under the best microscopes it looks perfectly homogeneous, which shows the very fine state of division of the platinum. Indeed, the platinum particles must be smaller than the wave-length of light.

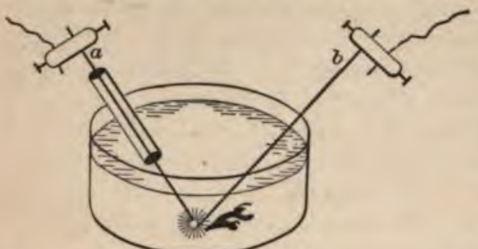

FIG. 31. BREDIG'S APPARATUS FOR PREPARING COLLOIDAL SOLUTIONS.

Bredig and Von Berneck found that this liquid has quite remarkable properties. It decomposes hydrogen dioxide like organic ferments, and resembles the latter in many other particulars. A gram atomic weight of platinum in 70,000,000 l. of water decomposes hydrogen dioxide appreciably, thus resembling organic ferments where a very small quantity can effect a large amount of decomposition. An even more striking analogy between the action of the colloidal platinum and organic ferments is to be found in the effect of certain poisons upon both of them. A very small amount of certain substances will entirely destroy the activity of organic ferments. Exactly the same was found to be the case with the colloidal solution of platinum. A gram-molecular weight of hydrocyanic acid in 1,000,000 l. of water diminished quite appreciably the activity of the colloidal platinum toward hydrogen dioxide; and a gram-molecular weight of hydrogen sulphide in 345,000 l. of water greatly diminished the activity of the platinum. A gram-molecular weight of hydrogen sulphide in 34,500 l. almost destroyed the activity of the platinum.

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[1] *Amer. Journ. Science*, **37**, 476 (1889); **38**, 47, 129, 237 (1889).

[2] *Ztschr. phys. Chem.* **31**, 258 (1899).

[3] *Ztschr. f. angew. Chem.* 1898, 951. *Ztschr. f. Elektrochem.* **4**, 514 (1897).

However close the relation between these colloidal solutions of the metals and organic ferments may be shown to be, this recent work has given an entirely new interest to the subject of colloidal solutions in general.

COLOR OF SOLUTIONS

Color of Solutions of Non-electrolytes. — If we are dealing with non-electrolytes, *i.e.* substances which exist in solution entirely as molecules, it is obvious that the color of such solutions is the color of the dissolved molecules, provided, of course, that the solvent is colorless. The color of such solutions resolves itself then into the question of the color of the molecules themselves. Our knowledge in this field is not yet sufficient to enable us to deal with this problem satisfactorily; yet it is quite certain that the color of molecules is due primarily to the nature of the chemical atoms which enter into the molecules. That constitution also has an influence is made clear by many facts which are known.

The problem, however, which is of special interest here, deals not with the color of molecules but with the color of ions; *i.e.* with the color of solutions of dissociated substances.

Color of Solutions of Electrolytes. — The problem of the color of solutions of electrolytes is simpler, and of more interest from our standpoint at present, than the problem with non-electrolytes. If the electrolyte is completely dissociated, *i.e.* completely broken down into ions, it is obvious that the color of such solutions is not due to the color of molecules, since there are no molecules present. The color of such solutions is due to the ions present, and to these alone.

Some of the consequences of this conclusion from the theory of electrolytic dissociation are very interesting. If we have a number of compounds containing say colorless anions combined with the same colored cation, the solutions of all of these substances should have the same color. Thus, take the salts of cobalt with colorless acids, the chloride, sulphate, nitrate, acetate, etc., dilute solutions of all of these salts should have the same color, and that the color of the cobalt ion, since such solutions are completely dissociated and the anion in each case is colorless. Here the facts confirm the theory. All such salts have exactly the same color in dilute solutions.

Conversely, if we have colorless cations combined with a colored anion, the solutions of the compounds formed should have the same color. This problem has been very thoroughly investigated by Ostwald.[1] He prepared solutions of a number of salts of permanganic acid with colorless cations, such as potassium, sodium, ammonium, lithium, barium, magnesium, aluminium, zinc, cadmium, etc., and then studied the absorption spectra. If our theory is correct, solutions of all of these substances should have the same color, which is to say that they should all have the same absorption bands. These bands were both carefully measured and photographed by Ostwald. These salts show five absorption bands in the yellow and green, and four of these were measured for thirteen salts of permanganic acid. The results of Ostwald's measurements are given in the following table: —

PERMANGANATES. ABSORPTION BANDS

	I	II	III	IV
Hydrogen	2601 ± 0.5	2698 ± 0.8	2804 ± 0.7	2913 ± 1.7
Potassium	2600 ± 1.3	2697 ± 0.1	2803 ± 0.9	2913 ± 1.1
Sodium	2602 ± 1.2	2698 ± 0.8	2803 ± 0.7	2913 ± 0.8
Ammonium . . .	2601 ± 1.3	2698 ± 1.4	2802 ± 0.1	2913 ± 0.1
Lithium	2602 ± 0.2	2700 ± 0.2	2804 ± 0.8	2914 ± 1.7
Barium	2600 ± 0.9	2699 ± 0.8	2804 ± 0.6	2914 ± 1.3
Magnesium	2602 ± 0.8	2700 ± 0.6	2802 ± 0.7	2912 ± 1.8
Aluminium	2603 ± 0.4	2699 ± 0.9	2804 ± 0.9	2914 ± 0.7
Zinc	2602 ± 0.5	2699 ± 0.7	2802 ± 1.2	2912 ± 1.1
Cobalt	2601 ± 0.2	2698 ± 0.1	2803 ± 0.9	2912 ± 1.7
Nickel	2603 ± 0.5	2700 ± 0.7	2804 ± 0.7	2913 ± 1.8
Cadmium	2600 ± 0.1	2700 ± 0.2	2803 ± 0.8	2913 ± 1.4
Copper	2602 ± 1.2	2699 ± 0.1	2803 ± 0.9	2913 ± 0.8

Ostwald concluded from these results that the absorption spectra of all the thirteen salts are exactly the same, to within the limit of error of measurement.

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[1] *Ztschr. phys. Chem.* **9**, 579 (1892).

The spectra of ten of these salts were photographed, the one directly over the other, and the results are given in the accompanying figure. The agreement between the position and character of the bands is so striking, that there is no room for doubt that these salts show the same absorption bands.

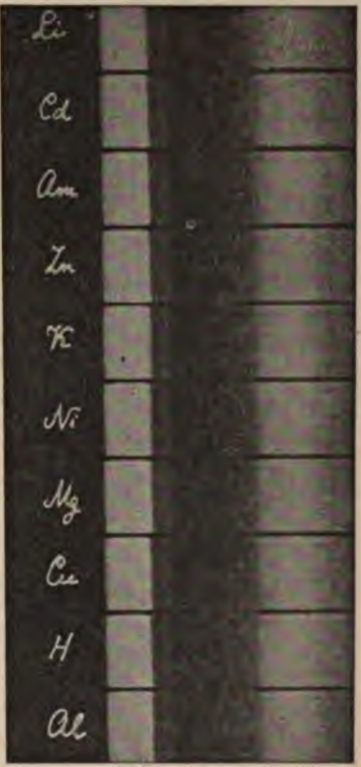


FIG. 32.

In addition to the permanganates Ostwald studied a number of classes of substances. The absorption spectra of ten salts of fluoresceïn were also photographed. The bands here agree as closely in position and nature as with the permanganates. Salts of eosin yellow, eosin blue, iodoeosin, rozolic acid, diazoresorcin, etc., with colorless cations were made, and the absorption bands of each class of compounds compared. Then salts of colored bases with colorless acids were prepared and studied. These included especially p-rosaniline and aniline violet. The results with p-rosaniline are given below. The absorption band which was measured is in the yellow-green.

P-ROSANILINE, DILUTION 5600 L.

1. Levulinic acid . . .	2715 ± 0.8	**11.** Hyposulphuric acid .	2715 ± 1.1
2. Acetic acid	2715 ± 1.4	**12.** Trichlorlactic acid .	2715 ± 0.7
3. Chloric acid	2716 ± 0.4	**13.** Glycolic acid . . .	2714 ± 1.3
4. Benzoic acid	2714 ± 1.4	**14.** Phthalanilic acid . .	2716 ± 1.3
5. Hydrochloric acid . .	2714 ± 1.1	**15.** Perchloric acid . .	2715 ± 1.2
6. Sulphanilic acid . .	2715 ± 1.2	**16.** Salicylic acid . . .	2715 ± 1.5
7. Nitric acid	2715 ± 0.5	**17.** Monochloracetic acid	2715 ± 1.5
8. Phthalamodoacetic acid	2715 ± 1.4	**18.** Lactic acid	2715 ± 1.0
9. Butyric acid	2715 ± 1.3	**19.** *O* nitrobenzoic acid .	2715 ± 1.3
10. Phenylpropiolic acid .	2715 ± 0.9	**20.** Sulphuric acid . . .	2715 ± 0.9

These results were also photographed, and the absorption bands of these twenty salts are shown in Fig. 33. The figures have the same significance in the plates as in the tables. Ostwald's work included about 300 compounds, in some of which the cation was colored, while others contained a colored anion. He concluded from this elaborate investigation, that salts with one and the same colored ion, in dilute solutions, always have the same spectra. If both ions were colored, the color of the solution would be the sum of the colors of the two ions. The color of completely dissociated solutions is, therefore, an additive property.

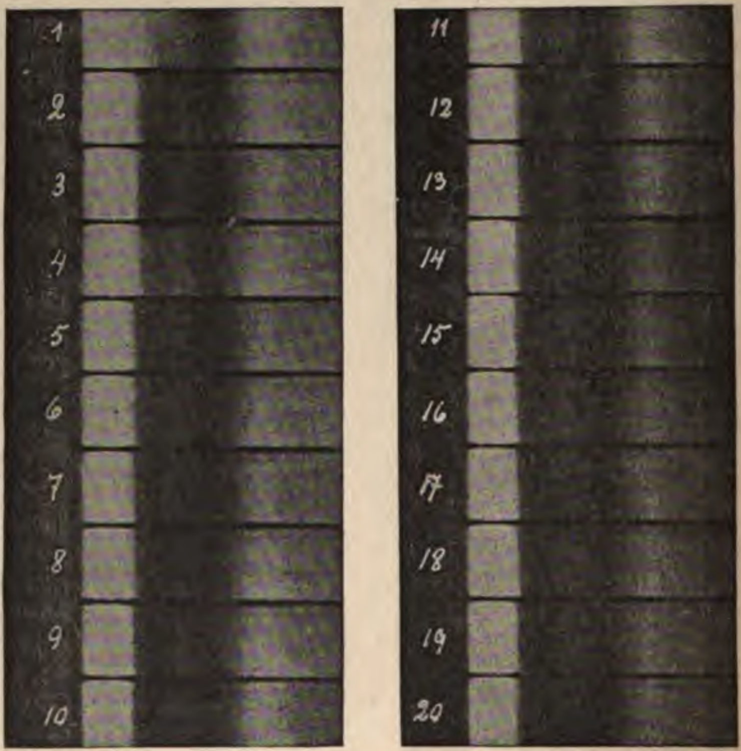


FIG. 33.

Change in Color with Change in Electrical Charge. — An ion having the same chemical composition does not always have the same color. Take the ion $Fe(CN)_6$; in potassium ferrocyanide it is yellow and gives the yellow color to a solution of this salt. The ion in this case is formed by the dissociation of the salt $K_4Fe(CN)_6$ into

$\overset{+}{K} + \overset{+}{K} + \overset{+}{K} + \overset{+}{K}$, and $Fe\overset{=}{(}CN)_6$, which carries four negative charges. The ion $Fe(CN)_6$, obtained by the dissociation of potassium ferricyanide, is red. The compound $K_3Fe(CN)_6$ dissociates as follows: $K_3Fe(CN)_6 = \overset{+}{K} + \overset{+}{K} + \overset{+}{K} + Fe\overset{\equiv}{(}CN)_6$. The ion $Fe(CN)_6$, in this case, carries three negative charges, and the difference of one charge changes the color of the ion from yellow to red.

Again, take the ion MnO_4. If it is formed by the dissociation of potassium permanganate, $KMnO_4$ ($KMnO_4 = \overset{+}{K} + M\overset{-}{n}O_4$), it is purplish red, and gives the characteristic color to a solution of this salt. If it is formed from potassium manganate,

$$K_2MnO_4 = \overset{+}{K} + \overset{+}{K} + M\overset{=}{n}O_4,$$

it is green. In the first case it carries one negative charge, in the second case two; and this difference in electrical condition produces a change in color from purple to green.

Finally, to take a simpler example: The iron ion in the ferrous condition is green, as is seen in solutions of ferrous salts; while the iron ion in the ferric condition is yellow, as is seen in solutions of ferric salts. An almost unlimited number of examples of changes in the color of ions with change in the electrical charge which they carry, might be given.

One other point should be mentioned in this connection. An element in the form of an ion may have its own definite characteristic color. When this element is combined with other elements to form a complex ion, the color of the complex may have no simple relation to that of the element when present alone as an ion. The cobalt ion is red. When combined with cyanogen to form a complex anion it is colorless. Thus the compound $K_3Co(CN)_6$ dissociates into

$$\overset{+}{K} + \overset{+}{K} + \overset{+}{K} + Co\overset{\equiv}{(}CN)_6,$$

and the solution of this compound is colorless. Here, also, many examples are available.

Theory of Indicators. — We have just seen that molecules may be colored, giving the characteristic color to solutions of undissociated substances; and that ions also may be colored, giving the color to completely dissociated solutions. A molecule may have the same color as the ions into which it dissociates, or it may have a different color. A colorless molecule may dissociate into ions, one or more of which is colored; and a colored molecule may dissociate into colorless ions.

Upon these facts is based the use of indicators in quantitative analysis. An indicator is a compound which shows a change of color when the solution passes from the acid to the basic condition, and *vice versa*. An indicator is always either a weak acid or a weak base, which, on dissociation, yields an ion which has a different color from the molecule itself. Indicators fall then, naturally, into two classes, — acidic indicators and basic indicators. As an example of an *acidic indicator*, we will take first *phenolphthaleïn*. This is a weak acid, which means that in the presence of water it is very slightly dissociated, if it is dissociated at all. The molecules of phenolphthaleïn are colorless, as is shown by the fact that an aqueous or alcoholic solution of this substance is colorless. If a solution of a strong base is added to phenolphthaleïn, the salt of that base is formed. This salt, like most salts, is readily dissociated in the presence of water. The salt of phenolphthaleïn dissociates into the cation of the base and the complex organic anion; *e.g.* the sodium salt dissociates into the cation sodium and the complex organic anion; and it is this latter which gives the characteristic color of this indicator.

In using this indicator, a small quantity is brought into the presence of the acid, which is to be titrated against a strong base. The indicator, in the presence of pure water, is almost completely undissociated. In the presence of the strong acid which contains many free hydrogen ions, it would be dissociated even less than in pure water, as we shall learn. An alkali is added and the strong acid is all neutralized. The moment an excess of alkali is present, it forms a salt with the phenolphthaleïn. This salt dissociates at once, and the colored anion gives its characteristic color to the solution.

Phenolphthaleïn cannot be used with weak acids nor weak bases. If the acid is so weak that its salts, even with strong bases, are *hydrolyzed*, *i.e.* broken down by water into the free acid and the free base, the free base would begin to react with the phenolphthaleïn long before enough base had been added to completely neutralize the acid. The result would be the appearance of a faint color on the addition of a little alkali, and this color would increase in intensity as more and more alkali was added. There would, then, be no sharp change in color when all the acid had been neutralized, and the indicator would be practically worthless in such cases. Thus, carbonic and phosphoric acids and the phenols cannot be titrated with phenolphthaleïn as an indicator. If a weak base is used, such as ammonia, there will also be a certain amount of hydrolysis of the salt. This will leave some free base present, which will react with the phenolphthaleïn and give rise to a gradual change in color. But even if the ammonium salt of the acid which is being titrated is not hydrolyzed by water, ammonia cannot be used with phenolphthaleïn. Ammonia is a weak base, and phenolphthaleïn is a weak acid, and the salt of the two would itself be hydrolyzed by water. The indicator would, therefore, not act sharply when ammonia was used as a base.

It is well known that the facts agree very satisfactorily with the theory. Phenolphthaleïn cannot be used as an indicator with either weak acids or weak bases.

Another example of an acid indicator whose molecules are nearly colorless and whose anion is colored, is *p-nitrophenol*. In alcoholic solution, in which the substance is almost undissociated, it is nearly colorless. Water dissociates it slightly, and consequently the aqueous solution is slightly colored. If an alkali is added, the salt of this weak acid is formed, and this dissociates into the metallic cation and into the anion $C_6H_4(NO_2)O$, which is deep yellow in color. The action of this substance as an indicator will be understood at once from the above description of the action of phenolphthaleïn.

Litmus is an example of an acid indicator whose molecules are colored, but whose anion has a different color. The molecules of the weak litmus acid are red. When an alkali is added, the salt is formed, and this dissociates giving the free litmus anion, which is deep blue. Litmus, like phenolphthaleïn, cannot be used satisfactorily with weak bases. These would form salts with the litmus, which would be hydrolyzed and prevent a sharp color reaction; or their salts, with any but the strongest acids, would undergo some hydrolysis and prevent a sharp appearance of color. In order that litmus should be used in titrating weak acids, only the strongest bases can be employed.

An acid indicator which can, however, be used with weak bases is *methyl orange*. This is a considerably stronger acid than the indicators which we have already considered. The molecules of the free acid are red, the anions yellow. In the presence of a strong acid we have, therefore, the characteristic red color; while in the presence of a base the salt is formed, and this dissociates, yielding the yellow anion. This indicator can be used with weak bases, provided they are titrated with strong acids. In these cases there is but slight hydrolysis of the salts formed, and also but slight hydrolysis of the salt formed by the methyl orange and the weak base, since the indicator is a fairly strong acid.

In the above discussion of acid indicators it will be seen that weak acids must always be titrated with strong bases, and a weakly acid indicator may be employed.

Weak bases, on the other hand, must be titrated with strong acids, and a strongly acid indicator must be employed.

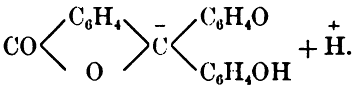
Basic indicators are but little used in practice. As an example of this class we may take *cyanine*. This is a weak base, and therefore but little dissociated. The molecules are deep blue in color. In the presence of an acid a salt is formed, which dissociates into the anion of the acid and the cation of the base. This very complex cation is colorless; consequently the indicator is blue in the presence of a base, and colorless in the presence of an acid.

The examples considered above suffice to illustrate the different types of indicators, and to show how satisfactorily their action is explained in terms of the theory of electrolytic dissociation.

A Color Demonstration of the Dissociating Action of Water. — Jones and Allen[1] have worked out a color demonstration of the dissociating action of water, which is based upon the principle of indicators just considered. If to an alcoholic solution of phenolphthaleïn a few drops of aqueous ammonia are added, there is no sign of the red color of the indicator. If water is now added to the alcoholic solution, the red color appears. When potassium or sodium hydroxide is substituted for ammonia, the red color appears at once, without the addition of water. There is thus a marked difference between potassium or sodium hydroxide, and ammonium hydroxide.

It would be difficult to interpret these facts without the aid of the theory of electrolytic dissociation. In the light of this theory they are perfectly intelligible.

When a few drops of aqueous ammonia are added to several cubic centimetres of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water dissociates the base, the degree of dissociation depending upon the amount of water present with respect to alcohol. The presence of the ions $\overset{+}{NH_4}$ and $\overset{-}{OH}$ would cause the phenolphthaleïn to dissociate into —



The complex anion gives its characteristic color to the solution in which it is present. The hydrogen and hydroxyl ions would then combine and form water.

It is possible that the actual course of the reaction is somewhat different from that just described. It may be that the ammonium first combines with the phenolphthaleïn in the alcoholic solution. The addition of water would then dissociate this compound, giving the colored anion referred to above.

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[1] *Amer. Chem. Journ.* **18**, 377 (1896).

The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true.

If it is, then a solution formed by adding a little aqueous ammonia to a considerable volume of alcohol, should show little or no dissociation, and the amount of the dissociation should increase with the addition of water. Solutions of potassium or sodium hydroxide, in mixtures of alcohol and water, should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide in alcohol alone should manifest some dissociation, since, as stated above, it gives the color reaction with phenolphthaleïn.

All of these points were tested experimentally by the conductivity method, with the result that the theory of electrolytic dissociation was confirmed at every point.

This experiment furnishes a satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthaleïn are placed in a glass cylinder and diluted to, say, 50 c.c. by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthaleïn, but this will disappear instantly on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthaleïn. Water is then gradually added to the cylinder, when the red color will appear, at first faint, then stronger, as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol, and the entire color will disappear, leaving the solution slightly yellow again.

Fluorescence and Dissociation.—Closely connected with the color of solutions is the fluorescence shown by certain substances in solution. When a substance like fluoresceïn is brought into the presence of water, it dissolves to only a slight extent, and the solution formed is only slightly fluorescent. If to fluoresceïn in the presence of water a little alkali is added, an intense fluorescence appears at once. This is satisfactorily interpreted in terms of the dissociation theory. Fluoresceïn is a weak acid only slightly soluble in water, and very slightly dissociated by it. Being an acid, it would dissociate into a hydrogen cation and a complex organic anion.

The hydrogen cation is evidently not fluorescent, since all acids yield hydrogen cations as one of the products of dissociation, and solutions of acids in general are not fluorescent. The fluorescence of fluoresceïn must, then, be due to the complex organic anion formed as the product of dissociation of the fluoresceïn molecule.

If this is the true explanation of the fluorescence of this substance, then, if we could increase the dissociation of fluoresceïn by any means, we should increase the fluorescence, since we would increase the number of fluorescent ions present in the solution. This can be accomplished by adding an alkali, which forms a salt with the fluoresceïn. This, like all other salts, dissociates readily in the presence of water, and we have a large number of fluorescent ions formed; hence the increase in fluorescence on addition of an alkali.

It is sometimes stated that in this and similar cases we have the alkali salt formed, and it is this salt which is fluorescent as such. It should be stated here, that it has been shown that under such conditions there is not a trace of the alkali salt of fluoresceïn present in the solution, if the solution is very dilute. It can be shown by any of the well-established methods for measuring dissociation, that all of the salt present is broken down into ions and that there are no molecules in the solution. If there are no molecules present in the solution but only ions, it is obvious that the fluorescence can be due only to the ions.

The earlier explanation that the phenomenon observed here, and also the phenomena observed with indicators, were due to the formation of alkali salts, and that these persisted as such in the solutions, giving the characteristic properties, has given way in the light of the discoveries of modern physical chemistry. We now know that in all such cases we are dealing not with molecules as such, but with the ions into which they dissociate.

OTHER PROPERTIES OF SOLUTIONS

Properties of Solutions of Non-electrolytes. — In dealing with the properties, in general, of solutions, we must clearly distinguish between solutions of undissociated and of dissociated substances. If we are dealing with the former class, the dissolved substances exist only in the molecular condition, and it is obvious that all of the properties are the properties of the dissolved molecules plus those of the solvent. If we are dealing with aqueous solutions, the properties of water being so well known, we can easily determine what are the properties of the dissolved substance.

Properties of Solutions of Electrolytes. — If we are dealing with electrolytes, the problem is very different. The molecules are more or less broken down into ions, and at very high dilutions all the molecules are dissociated into ions. The properties of such solutions are obviously not the properties of molecules, since there are no molecules present, but the properties of the ions, which are the only units present in the solution. In terms of the theory of electrolytic dissociation, the properties of completely dissociated solutions are the sum of the properties of all the ions present in the solution — are additive. We have seen that this is true in the case of color; we shall see in a moment how it applies to other physical properties. Meanwhile, a word in reference to the chemical properties of completely dissociated solutions.

Chemical Properties of Completely Dissociated Solutions. — The chemical properties of solutions which contain only ions must be the chemical properties of the ions present. Some surprising facts, however, come out when we study the chemical properties of ions. An element in the ionic state has certain definite characteristic properties. These properties bear no close relation to those of the same element in the atomic or molecular condition. Take the element which has often been cited in this connection — chlorine. One of the most characteristic reactions of the ion chlorine is the formation of silver chloride by combining with the ion silver. Chlorine in the molecular condition, as in the form of gas, or even when freshly dissolved in water, does not precipitate a solution of silver nitrate. Further, chlorine in compounds like CH_3Cl, C_2H_5Cl, etc., is not precipitated by silver nitrate, because these compounds are not dissociated by water, and the chlorine is, therefore, not in the ionic condition.

Again, chlorine may even exist in the ionic condition and not be precipitated by silver nitrate, if it is in combination with other elements, forming a complex ion. Thus, the chlorine in potassium chlorate is not precipitated by silver nitrate, although the chlorine forms part of an ion. Potassium chlorate dissociates thus: —

$$KClO_3 = \overset{+}{K} + \overset{-}{ClO_3}.$$

The chlorine is present in combination with oxygen, forming an anion, but it has lost its most characteristic property, due to the presence of the oxygen.

Another example will illustrate the same point. The most characteristic reaction of the ion $\overset{=}{SO_4}$ is its power to combine with the ion $\overset{++}{Ba}$ and form barium sulphate. If the ion $\overset{=}{SO_4}$ is in combination with a complex group, it may not precipitate barium sulphate at all. Thus, if sulphuric acid and alcohol are warmed together there is formed the compound $\begin{matrix}C_2H_5\\H\end{matrix}\Big\rangle SO_4$, ethyl-sulphuric acid. This, like all acids, dissociates into a hydrogen cation, and the remainder of the compound forms the anion — in this case $\overset{-}{C_2H_5SO_4}$. When a solution of ethyl-sulphuric acid is treated with barium chloride, no precipitate is formed.

These examples suffice to show with what care we must judge of the chemical properties of substances under different conditions, knowing their properties under any one set of conditions.

Physical Properties of Completely Dissociated Solutions. — That the physical properties of completely dissociated solutions are, in general, additive, will be seen from a brief account of some of the work which has been done on solutions of salts. Only a few physical properties will be considered.

The *densities of solutions* of a number of salts have been studied by J. Traube. When a salt is added to water, there is produced a change in volume. If the salt is completely dissociated by the water, this change must be the sum of the changes produced by all the ions present.

If we represent by d the density of a solution containing a gram-molecular weight of salt having a molecular weight M, in g grams of water, and the density of pure water by d_0, we have an increase in volume Δv: —

$$\Delta v = \frac{M+g}{d} - \frac{g}{d_0}.$$

The following changes in volume will show the additive nature of this property: —

		Diff.		
KCl	26.7	9.0	NaCl	17.7
	(8.4)			(9.0)
KBr	35.1	8.4	NaBr	26.7
	(10.3)			(9.4)
KI	45.4	9.3	NaI	36.1

The differences between the halogens are practically constant whether they are combined with potassium or sodium. Similarly, the differences between the alkalies are constant, regardless of the nature of the halogen with which they are combined.

The *change in volume in neutralization* has given some interesting results in the hands of Ostwald.[1] He measured the volume changes produced by neutralizing potassium, sodium, and ammonium hydroxides with a large number of acids. The solutions contained a gram-equivalent of the substance in a kilogram. The changes in volume are expressed in cubic centimetres.

	KOH	Diff.	$NaOH$	Diff.	NH_4OH	Diff.
Nitric acid	20.05	0.28	19.77	26.21	−6.44	26.49
	(0.53)		(0.53)		(0.13)	
Hydrochloric acid . .	19.52	0.28	19.24	25.81	−6.57	26.09
	(0.42)		(0.43)		(0.13)	
Hydrobromic acid . .	19.63	0.29	19.34)	25.91	−6.57	26.20
	(10.53)		(10.49)		(9.82)	
Acetic acid	9.52	0.24	9.28	25.54	−16.26	25.78
	(11.78)		(11.64)		(11.30)	
Lactic acid	8.27	0.14	8.13	25.87	−17.74	26.01
	(8.15)		(8.29)		(7.91)	
Sulphuric acid . . .	11.90	0.42	11.48	25.83	−14.35	26.25
	(11.82)		(11.84)		(11.19)	
Succinic acid	8.23	0.30	7.93	25.56	−17.63	25.86
	(10.64)		(10.53)		(10.52)	
Tartaric acid	9.41	0.17	9.24	26.20	−16.96	26.37

The differences all refer back to nitric acid as the standard. They are the same for two different bases when neutralized with the same acid, regardless of the nature of the acid; as is shown by the practically constant value of the "differences" in each vertical column.

The differences are also the same when any given acid is neutralized by a number of bases, independent of the nature of the base; as is shown by the constant value of the bracketed numbers in horizontal rows.

The minus values for ammonia mean contraction in volume; the positive values in the other two cases mean that there is an expansion in volume.

The *refractive power* of strongly dissociated solutions has been studied especially by Gladstone[2] and Le Blanc.[3] The former showed that the refraction equivalents of two salts of different metals was independent of the nature of the acid with which the metals were combined. And the converse was also true; that the refraction equivalents of two salts of different acids was independent of the nature of the base with which the acids were combined. In a word, we have in refractivity a distinctly additive property — the refractivity being the sum of two constants, one depending upon the acid and the other upon the base.

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[1] *Jour. prakt. Chem.* [2], **18**, 353 (1878).

[2] *Phil. Trans.* 1868. Kanonnikoff: *Jour. prakt. Chem.* [2], **31**, 321 (1885).

[3] *Ztschr. phys. Chem.* **4**, 553 (1889).

Optical activity, or the power of salt solutions to rotate the plane of polarized light, was shown by Landolt[1] to be an additive property. Completely dissociated solutions of salts containing an optically active ion showed the same rotatory power, if the concentrations are the same. This was confirmed by the work of Oudeman.[2] He found also that alkaloids show the same rotatory power for equal concentrations, independent of the nature of the optically inactive acid with which they are combined; and further, that optically active acids show the same rotatory power, independent of the nature of the inactive base combined with them.

In a similar manner it has been shown by Becquerel, Perkin,[3] and especially by Jahn,[4] that the *magnetic rotatory* power of completely dissociated solutions is an additive property.

A number of other properties of completely dissociated solutions have been shown to be additive; such as *surface-tension, inner friction, heat expansion, lowering of freeezing-point, lowering of vapor-tension,* etc. But those considered above are quite sufficient to show that the properties of completely dissociated solutions are, in general, additive, — the sum of two constants, — the one depending upon the anion, the other upon the cation.

Additive Properties and the Theory of Electrolytic Dissociation. — The agreement between this large mass of facts and the theory of electrolytic dissociation is a strong argument in favor of the general correctness of the theory. The importance of this line of argument for the theory was early recognized, and was pointed out clearly and at some length by Arrhenius[5] when he proposed the theory of electrolytic dissociation. He then took up a number of the properties which we have considered in this section, and, in addition, other physical properties of solutions which it would be premature to consider in this place.

These facts not only fall in with the theory of electrolytic dissociation, but it is difficult to see at present how they can be interpreted in terms of any other theory. The fact that the physical properties of dilute solutions of electrolytes are additive, — *i.e.* the sum of two constants, — would certainly indicate that the two parts of the compound enjoyed an independent existence in the solution; or at least an existence so nearly independent that each had but little influence on the other. This is at once apparent when we consider that the properties of each part of the compound manifest themselves as if it alone were present. But independent existence of the ions is but another name for the theory of dissociation.

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[1] *Ber. d. chem. Gesell.* **6**, 1073 (1873).

[2] *Beibl. Wied. Ann.* **9**, 635 (1885).

[3] *Jour. Chem. Soc.* **55**, 680 (1889).

[4] *Wied. Ann.* **43**, 280 (1891).

[5] *Ztschr. phys. Chem.* **1**, 631 (1887).

SOLUTIONS IN SOLIDS

Solutions of Gases in Solids. — Many solids have the property of dissolving gases in large quantities. Thus, charcoal dissolves large volumes of carbon dioxide, palladium hydride dissolves hydrogen, etc. Our knowledge of such solutions is almost limited to the fact that they exist. It is known, however, that the greater the pressure to which the gas is subjected, the larger the quantity which will be absorbed by the solid. In speaking of solutions of gases in solids we mean, as in all other cases of true solution, those in which there is no chemical action between the gas and the solvent. The fact that gases can form solutions in solids is often utilized to remove the gas from regions where it is not desired. The solubility of a gas in a solid may be very great, indeed, as in the case above mentioned of carbon dioxide in charcoal.

Solutions of Liquids in Solids. — It is well known that solids have the general property of taking up many liquids in greater or less quantities. The great difficulty in obtaining solids free from water might be taken as an example. Our knowledge of the properties of such solutions is really limited to their existence. This is due to the fact that such solutions have been very little studied, owing in part to the difficulties involved in dealing with them. In solutions of liquids in solids it is difficult to say just when chemical action between the two ceases, and true solution begins. Our lack of knowledge in this field is also partly due to the fact that the conceptions of modern physical chemistry are so new that sufficient time has not yet elapsed to push the studies, in terms of these conceptions, into remote fields. That there is much which can be learned in reference to solutions of liquids in solids, will probably be shown in the not very distant future.

Solutions of Solids in Solids. — Here our knowledge is much more satisfactory than in either of the cases which we have just considered. Indeed, a study of this subject will show how interesting facts become when some one has pointed out their meaning and importance. Little or nothing was heard of solid solutions until Van't Hoff[1] published his now well-known paper about eleven years ago.

When electrolytes are dissolved in water, they give abnormally large depressions of the freezing-point of the solvent. To account for this and allied phenomena, the theory of electrolytic dissociation was proposed. When some other substances are dissolved in solvents other than water, they give *abnormally small depressions of the freezing-point.* This could be explained by assuming the presence of complex molecules of the substance dissolved. If this assumption is true, then, as the dilution is increased, the complex molecules should gradually break down into single molecules, and for very dilute solutions the molecular lowering found, for such substances should agree with the theoretical value. But the largest value obtained experimentally for the molecular depression was considerably smaller than the calculated.[2] This led Van't Hoff to suspect that when certain solutions are frozen, the solid which separates is not the pure solvent, but a *mixture of the solvent and the dissolved substance forming a solid solution.* The facts known at that time which bore on this point were then considered by Van't Hoff in the paper above cited.

If a solid solution is a solid, homogeneous complex of several substances, in which the properties can change without destroying the homogeneity, then examples are known. In isomorphous mixtures, as the alums, there is miscibility in all proportions, corresponding to completely miscible liquids. Another example is the formation of "mixed crystals," which are to be distinguished from double salts, and by their chemical composition show no isomorphism. Ammonium chloride forms such crystals with the "ous" chlorides of iron, manganese, nickel, etc. Ferric chloride is taken up by ammonium, calcium, lithium, etc., chlorides. When enough ferric chloride is present, the first two form also a double salt, which can be distinguished from the mixed crystal. Further, there are many colored minerals known in which the ground mass is colorless. Yet, optical investigations have shown them to be completely homogeneous. There are many amorphous, solid solutions, as the glasses and hyaline minerals.

Spring[3] has furnished the following interesting example, showing the mutual solubility of solids. When an equimolecular mixture of barium sulphate and sodium carbonate are pressed together, a double decomposition, amounting to even 20 per cent, takes place. That an equilibrium should be established, is conceivable only on the assumption that with the solids we have a partial miscibility.

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[1] "Ueber feste Lösungen und Molekulargewichtsbestimmung an festen Körpern," *Ztschr. phys. Chem.* **5**, 322 (1890).

[2] Eykman: *Ztschr. phys. Chem.* **4**, 497 (1889).

[3] *Bull. Soc. Chim.* **44**, 166 (1885).

Properties of Solid Solutions. — If solid solutions are a reality, then we would expect to find at least some of the properties of gaseous and liquid solutions manifested to a greater or less degree. Such is the case. The *diffusion* of a solid through a solid has been demonstrated. When barium sulphate and sodium carbonate were pressed together, and the pressure removed, the transformation continued, and in seven days amounted to from 73 to 80 per cent. Diffusion must have come into play here; slow, it is true, but this would be anticipated, since a gas diffuses through a gas far more rapidly than a liquid through a liquid.

A more striking example of diffusion in solids where no chemical action comes into play, is the penetration of hot porcelain by carbon. Marsden[1] proved that when a porcelain crucible is heated in graphite, the carbon completely penetrates the porcelain. Further, zinc objects covered with a thin layer of copper become gradually white, due, as analysis has shown, to a gradual increase of zinc in the copper. This illustrates the diffusion of solid in solid at ordinary temperatures. Van't Hoff has thus furnished examples illustrating beyond question the diffusion of solid through solid. Other examples of the diffusion of one metal through another have been furnished by Spring.[2] But, perhaps, the most striking example of the diffusion of one metal through another has been recently furnished by Roberts-Austen.[3] Disks of gold were clamped to the bases of lead cylinders, and allowed to remain standing for four years. The bases of the lead cylinders were carefully smoothed and the disks of gold especially cleaned. These were then placed in a vault, whose temperature was practically constant at 18° C. At the end of four years it was found that the disks of gold had adhered to the lead. Slices were cut from the lead cylinders at right angles to the axes of the cylinders, and these were then assayed for gold. It was found that the gold had penetrated about 8 millimetres into the lead; the gold being more concentrated in that portion of the lead disk which was in contact with the gold plate, as we would expect. In liquids we seek the cause of diffusion in *osmotic pressure*. May not the diffusion of solid through solid be of *like origin?* From the nature of solid solutions it seems to be impossible to determine this directly. The work of Colson,[1] however, on the diffusion of carbon in iron has made it probable that a proportionality exists between the amount of diffusion and the concentration, as with liquid solutions whose osmotic pressure obeys Boyle's law.

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[1] *Proc. Edinb. Soc.* **10**, 712.

[2] *Rapport Congres International de Physique*, I, 412, Paris, 1900.

[3] *Proc. Roy. Soc.* **67**, 101 (1900).

The simplest connection between Boyle's law and the other laws of osmotic pressure is the law of Henry. If this applies to solid solutions, gases must be dissolved by solids in proportion to the gaseous pressure. Take the case of the absorption of hydrogen gas by palladium.[2] When the hydrogen is kept at 225 mm. pressure and 100°, the palladium will take up a quantity corresponding to the compound Pd_2H. No further absorption of the gas will take place unless the pressure is increased. After the compound Pd_2H is formed, further absorption of the hydrogen results in the formation of a solid solution. For our consideration only the hydrogen which forms a solid solution comes into play.

Let P represent the pressure of the gas, and let V represent the volume of the gas absorbed. If we divide the pressure by the total volume absorbed, minus that volume which was taken up to form the compound Pd_2H (in this case 600), we have: —

V	P	$\frac{P}{V-600}$	V	P	$\frac{P}{V-600}$
809	1428	6.8	775	715	4.1
743	909	6.4	743	493	3.5
700	598	6.0	718	361	3.0
672	454	6.3	684	247	3.0
642	353	8.4			
Palladium which had been fused.			Palladium sponge.		

The value of $\frac{P}{V-600}$ is, in each case, as near a constant as could be expected from the nature of the experiments.

Since Henry's law holds, then, for solid solutions as well as for liquid, we have here also the *osmotic pressure equal to the gas-pressure* for the same concentration and temperature.

Another well-known fact in connection with a liquid solution is that its vapor-tension is less than that of the solvent. In solid solutions there is also a *diminution of the maximum tension of the solvent.*

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[1] *Compt. rend.* **93**, 1074.

[2] Troost and Hautefeuille: *Ibid.* 1874, 686.

Lead dithionate,[1] which decrepitates very easily, showing considerable tension, has this tension markedly diminished by forming with it an isomorphous mixture containing a small amount of the calcium or strontium salt. The same holds for iron alum, whose tension is diminished by the formation of an isomorphous mixture with aluminium alum.

This diminution in tension is not due simply to the addition of a constituent which has a smaller tension, since the tension of the mixture is less than that of either constituent.[2] This decrease in the tension of solid solutions manifests itself in the decrease of solution-tension, causing a decrease in solubility. When saturated solutions of ammonium iron, and ammonium aluminium alums are brought together, an isomorphous mixture of both salts separates, showing a decrease in solution-tension or solubility, when the solid solution is formed. Such are some of the properties of solid solutions, and some of the analogies between these and liquid solutions.

Molecular Weights of Solids. — To determine the molecular weights of substances in the liquid condition we rely chiefly upon liquid solutions. May not solid solutions furnish us with methods for determining the molecular weights of substances in the solid state? There are two possibilities; the one having to do with the tension of the dissolved body; the other with that of the solvent.

If we are dealing with the tension of the dissolved body, the problem reduces itself to determining whether there is proportionality between the gas-pressure and the concentration of the solid solution formed — whether in any given case Henry's law holds. If it does, the dissolved gas has the same molecular weight as the free gas. Thus, hydrogen dissolved in palladium hydride, forming a solid solution, has a molecular weight corresponding to H_2. Were it H_3 or H, the values of $\frac{P}{V-600}$ would have been much farther removed from a constant.

The second method deals experimentally with the relation between the composition of the solid solution, and the liquid solution from which it was formed. If the dissolved body has the same molecular weight in both solutions, this relation must be constant. To determine the molecular weight of, say, thiophene in the solid condition, prepare two solutions of known concentration of thiophene in benzene. When these are frozen, a solid solution of thiophene in benzene will separate in each case. If an analysis of the solid shows a constant proportionality between the amount of thiophene in the solid and liquid solutions, the thiophene has the same molecular weight in the solid as in the liquid form.

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[1] Von Hauer: *Verhand. d. k. k. geol. Reichsanstalt*, 1877, 163.

[2] Lehmann: *Molekularphysik*, **2**, p. 57.

THIOPHENE IN BENZENE

PER CENT P	DEPRESSION FOUND	NORMAL DEPRESSION	DIFFERENCE D	$\frac{D}{P}$
0.847	0°. 34	0°.535	0°.195	0.230
2.10	0°. 82	1°.325	0°.505	0.240
2.84	1°.085	1°.790	0°.705	0.248
3.63	1°.385	2°.290	0°.905	0.249

Under normal depression is the lowering which would have been produced had no solid solution been formed. Since the composition of the crystals which separated was not determined, the molecular weight of solid thiophene could not be calculated. The fact, however, that $\frac{D}{P}$ is a constant, makes it probable that the percentage of thiophene in the solids which separated, was proportional to that in the solutions. If so, thiophene would have the same molecular weight in the solid as in the liquid solutions.

Compounds which can form Solid Solutions with One Another. — Since the first fundamental paper appeared on solid solutions, by Van't Hoff, the study of such solutions has been devoted to two general problems: The relation between the chemical constitution of those compounds which can form solid solutions with one another, and the determination of the molecular weight of solids in solid solutions.

Most of our knowledge on the first-mentioned problem we owe to Ciamician and his colaborers, Garelli and Ferratini.[1] The object of this work was to test the chemical relations between substances which are necessary, in order that a solid solution may be formed when a solution of one in the other was frozen. It was already known that phenol, pyrrol, thiophene, pyridine, and piperidine, dissolved in benzene, gave abnormally small depressions of the freezing-point. This would indicate that solid solutions are formed only between those substances which have similar chemical constitution; but the data were too meagre to establish finally any such relation. The paper first cited deals only with cyclic compounds; the solvents used being benzene, naphthalene, phenanthrene, and diphenyl. To determine whether a solid solution was formed, the freezing-point method was used. Whenever a solid solution of the dissolved substance and the solvent separated, the freezing-point lowering would be abnormally small. It was shown that the following substances form solid solutions with the solvent indicated just above in italics: —

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[1] *Ztschr. phys. Chem.* **13**, 1 (1894); **18**, 51 (1895).

Benzene.

Thiophene, pyrrol, pyridine, pyrroline, and piperidine.

Naphthalene.

Indol, indine, quinoline, isoquinoline, and tetrahydroquinoline.

Phenanthrene.

Carbazol, anthracene, acridine, and hydrocarbazol.

Diphenyl.

Dipyridyl and tetrahydrodiphenyl.

Indol and indene in benzene give normal freezing-point lowerings; the same holds for carbazol or anthracene in benzene or naphthalene — these substances forming solid solutions with phenanthrene. That these abnormally small depressions of the freezing-point were due to the formation of solid solutions was established in a number of cases by direct experiment. From these results it would seem that only those substances are capable of forming solid solutions with one another which have *a cyclic structure of the same order;* benzene being an example of the first order, naphthalene of the second, and anthracene of the third.

That the chemical character of a compound, other than its cyclic structure, can have little to do with its power of forming solid solutions, is shown by the fact that compounds as different as pyrrol and pyridine manifest the same general cryoscopic behavior with benzene.

It will be seen from the foregoing that the formation of solid solutions consists in the dissolved substance and the solvent crystallizing out of the solution together. This being the case, it is not impossible that the relation between the crystallographic forms of the two substances may play a prominent part in determining what substances can form solid solutions with one another. Certain relations have already been pointed out[1] between the crystallographic constants of those substances which can form solid solutions. Here, however, partly on account of crystallographic difficulties, the data at hand are far too few for purposes of generalization. A second paper,[2] dealing with this part of the subject, furnishes further data which substantiate essentially the conclusions arrived at in the first. It may, then, be stated that in the ring compounds agreement in cyclic order seems to be necessary in order that solid solutions may be formed. It, however, does not follow, and it is not true, that solid solutions are formed whenever such an agreement exists.

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[1] Ciamician: *Ztschr. phys. Chem.* **13**, 6 (1894).

[2] Garelli: *Ibid.* **18**, 51 (1895).

Work of Küster on the Molecular Weights of Solids. — Considerable work on the second problem — the molecular weights of substances in solid solutions — has been done recently by Küster.[1] He studied at first the division of a given compound between two solvents which are practically insoluble in one another; the one being a liquid, the other a solid. The solvents chosen were water and pure caoutchouc. To these, in the presence of each other, ether was added and the quantity taken by each solvent determined. If the molecular weight of ether in the water was the same as in caoutchouc, when more and more ether was added to the solvents the quantity taken up by a given volume of the one, divided by the quantity taken up by the same volume of the other, would be a constant. That this is true has been shown experimentally[2] by quantitative determinations of the division of a substance between two solvents, and is analogous to the law of Henry for gases.

The experimental problem for Küster was, then, the addition of varying amounts of ether to a given volume of water and a known weight of caoutchouc in the presence of each other, and the determination of the amount of ether taken in every case by each solvent. The same point would of course be reached by keeping the amount of ether constant, and changing the relative amounts of the two solvents. Both methods were employed. The total amount of ether used in any experiment was known. The amount which was taken by the water was determined by the lowering of the freezing-point of the water produced by the ether. The difference between these two quantities was the ether which had been taken up by the caoutchouc. Care was taken to construct a freezing-point apparatus which would prevent loss in ether by evaporation. The time required for equilibrium to be established between the ether and the two solvents was duly regarded, and was shown not to exceed three hours.

In the first series of experiments weighed amounts of caoutchouc were added to a known volume of water and of ether, and the freezing-points of the aqueous solutions of ether determined after equilibrium had been established in each case. Fifty cubic centimetres of water were used and 5 c.c. of ether. The results of this series are given below: —

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[1] *Ztschr. phys. Chem.* **13**, 445 (1894); **17**, 357 (1895).

[2] Jakowkin: *Ibid.* **18**, 585 (1895).

	CAOUT-CHOUC	E	Aw c.c.	Vw c.c.	Cw c.c.	Ak c.c.	Vk c.c.	Ck c.c.	$\frac{Ck}{Cw}$	$\frac{\sqrt{Ck}}{Cw}$
1	17.606	−1.265	3.41	53.41	6.38	1.59	20.62	7.71	1.21	0.435
2	10.188	−1.380	3.72	53.72	6.92	1.28	12.29	10.41	1.55	0.466
3	5.924	−1.510	4.07	54.07	7.52	0.93	7.33	12.69	1.69	0.473
4	2.724	−1.660	4.47	54.47	8.21	0.53	3.57	14.85	1.81	0.469

In the preceding table: —

E is the freezing temperature of the aqueous solution of ether;

Aw is the number of cubic centimetres of ether in the aqueous solution, calculated from the value of E;

Vw is the volume of the aqueous solution;

Cw is the volume concentration of the ether in the aqueous solution,

$$=\frac{100\,Aw}{Vw};$$

Ak is the ether in the caoutchouc, $= 5 - Aw$;

Vk is the volume of the caoutchouc solution of ether;

Ck is the volume concentration of the ether in the caoutchouc,

$$=100\,\frac{Ak}{Vk}.$$

The value of $\frac{Ck}{Cw}$ is not constant, but, as is seen in the table, increases as the amount of caoutchouc present decreases; showing that the molecular weight of the ether dissolved in the caoutchouc is greater than of that in the water.

Ether dissolved in water gives a normal molecular depression of the freezing-point, and has, therefore, the simplest molecular weight, which corresponds to the formula $C_4H_{10}O$. The ether molecule in the caoutchouc must consist of more than one chemical molecule. Since the values of $\frac{\sqrt{Ck}}{Cw}$ are very nearly constant, the molecular weight of ether in caoutchouc must, in part at least, be *double* the simplest molecular weight;[1] for, as we shall learn, the square root sign in this connection has that significance.

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[1] *Ztschr. phys. Chem.* **8**, 112 (1891).

In a second series of experiments the amount of water and of caoutchouc were kept constant, and the amount of ether changed. The value of $\frac{Ck}{Cw}$ increased with increase in the concentration of the ether, showing that more double molecules exist in the caoutchouc when the concentration of the ether is increased, as would be expected. In the most dilute solution of ether employed, it is calculated that only one-tenth of the ether in the caoutchouc exists as double molecules; while in the most concentrated solution of ether, about one-half of the molecules are double.

The effect of temperature on the division of ether between water and caoutchouc was also investigated. It was found that the water takes relatively more of the ether, the lower the temperature. The number of double molecules of ether in the caoutchouc, for a given amount of ether, is about three times as great at 0° as at 21°; showing an increase in the number of simple molecules with increase in temperature, as would be expected.

The Molecular Weight of a Pure Homogeneous Solid. — The work described up to this point has shown, according to Küster, that ether dissolved in caoutchouc consists partly of single and partly of double molecules; the number of double molecules increasing as the concentration of the ether increases, and as the temperature is lowered. This tells us, however, absolutely nothing as to the molecular weight of pure ether in the solid condition.

The second investigation[1] of Küster aims at a solution of the problem of the molecular weight of a pure substance when in the solid solution. In his original paper on solid solutions Van't Hoff included isomorphous mixtures. In these substances Küster concludes that the physical molecules of the solvent and of the dissolved substance must have like structure, and be composed of a like number of chemical molecules. If we could ascertain the molecular weight of one of the substances in the isomorphous mixture, we would, therefore, know the molecular weight of the other, which we can regard as the solvent.

The division of one constituent of the isomorphous mixture between the other (which we will regard as a solid solvent) and a liquid solvent, would, as seen above, throw light on the molecular weight of the constituent of the mixture first mentioned. It was difficult to find an isomorphous mixture which would fulfil the condition that only one constituent should be soluble in the liquid solvent. Küster, however, secured such in a mixture of naphthalene and β-naphthol. These compounds form a complete series of isomorphous mixtures with one another. Further, the β-naphthol was soluble in water, which was used as the liquid solvent, while the naphthalene was practically insoluble. The experimental work consisted, then, in determining the division of the β-naphthol between the water and the naphthalene. Isomorphous mixtures of β-naphthol and naphthalene of known composition were added in turn to measured volumes of water, and shaken with it until the water became saturated with the β-naphthol. The amount of β-naphthol present in the water in each case was then determined.

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[1] *Ztschr. phys. Chem.* **17**, 357 (1895).

If we represent the concentration of β-naphthol in the water by Kw, and the concentration of that which remains in the mixture by Km, we have —

$$\frac{\sqrt{Km}}{Kw} = C.$$

The values found experimentally vary from 11.8 to 20.8.

The author concludes, as with ether in caoutchouc, and for the same reason, that the β-naphthol in the isomorphous mixture has *twice* the molecular weight of that in the water. The molecular weight of β-naphthol in water has been shown to correspond to the simple formula $C_{10}H_8O$. β-naphthol in naphthalene has, then, the double molecular weight $(C_{10}HO_8)_2$.

β-naphthol forms isomorphous mixtures with naphthalene; therefore, the molecules of crystallized naphthalene and also of β-naphthol are to be expressed by the double formulas,

$$(C_{10}H_8)_2 \text{ and } (C_{10}H_8O)_2.$$

There are certain assumptions involved in this process of reasoning, so that the conclusion while interesting cannot be accepted as final.

We have studied examples of solutions of matter in every state of aggregation, in matter of the same and every other state. We shall now turn from the study of matter as such, to the study of other changes which always take place to some extent when substances react chemically. Thus, thermal changes always accompany chemical reaction. Again, if the reaction takes place under certain conditions marked electrical changes result.

It was early recognized that energy transformations of some kind frequently accompany the transformations of matter; but the attention of the earlier chemists was confined almost entirely to the study of the material changes which were effected by chemical reaction. The nature of the substances which enter into the reaction, and especially the nature of the products formed, furnished the chief problems for the chemist in the first half of the nineteenth century. During the latter half of the century, however, more and more attention was paid to the energy changes; especially to the amount of heat which is set free when substances react; and this continued until the new physical chemistry, in the last fifteen years of the century, showed the tremendous importance of these energy transformations. Indeed, we know now that it is almost impossible to overestimate their importance, since they are probably the cause of all chemical activity. Substances react chemically because of differences in the quantity and intensity of the chemical energy present in them. In studying energy changes we are then dealing with the real cause of reactions, and from the standpoint of the science of chemistry these are far more important than the material transformations which accompany them. The fundamental problems of chemistry will never be solved by a study of the material changes alone, since these are relatively the less important side of chemical phenomena; but only through elaborate investigation of the energy relations which obtain in systems before reactions, and in the products of the reaction. The remainder of our subject has to do largely with energy changes. The transformations of chemical energy into heat constitute the subject-matter of *Thermochemistry.*

Electrochemistry deals with the transformation of chemical energy into electrical, and of electrical into chemical.

The relations between chemical energy and light furnish the material of *Photochemistry.*[1]

We can also study the velocities with which chemical reactions take place, and the conditions of equilibrium in such reactions. These furnish the subject-matter of *Chemical Dynamics* and *Chemical Equilibrium.*

We may also measure the relative *Chemical Activities* of different substances.

We shall take up first the subject of thermochemistry.

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[1] These subjects are taken up in the above order, since in terms of our prevailing theories we deal first with heat, then with electricity, and finally with light.

CHAPTER VI

THERMOCHEMISTRY

DEVELOPMENT OF THERMOCHEMISTRY

Earlier Observations; Law of Lavoisier and Laplace. — It was very early observed that chemical reactions are accompanied by thermal changes. Sometimes heat is absorbed, but much more frequently it is given out. The qualitative observations were followed by quantitative measurements as early as the time of Robert Boyle. The first valuable measurements of the heat of reaction were made by Lavoisier and Laplace.[1] They measured the amounts of heat liberated in many chemical reactions, and also studied the thermal changes which take place within the living body. They arrived at the first important generalization in the field of thermochemistry.

The amount of heat which is required to decompose a compound into its constituents is exactly equal to that which was evolved when the compound was formed from these constituents.[2]

The Work of Hess. — Modern thermochemistry may be said to date from the time of Hess.[3] He discovered a fact whose importance for thermochemical study it is difficult to overestimate. Many chemical processes do not take place in one stage, but in several; and it was often difficult, not to say impossible, to deal with such from the thermochemical standpoint. Hess showed that *the heat evolved in a chemical process is the same whether it takes place in one or in several stages.* This principle, known as the "Constancy of the heat sum," made it possible to deal with a large number of reactions which otherwise would lie entirely out of the scope of thermochemical measurements. Take, for example, the burning of sulphur in oxygen. If we know the heat evolved when sulphur is burned in oxygen to form sulphur dioxide and the heat evolved when sulphur dioxide is burned to sulphur trioxide, we would know at once the amount of heat which would be evolved when sulphur was burned directly to sulphur trioxide, — it would be the sum of the above quantities. On the other hand, if we knew the heat evolved when sulphur is burned to the trioxide, and the heat evolved when the dioxide is oxidized to the trioxide, we would know the heat which would be set free when sulphur was burned to the dioxide, — it would be the difference between the above two quantities.

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[1] *Œuvres de Lavoisier*, II, 283.

[2] *Ibid.* II, 287.

[3] *Pogg. Ann.* **50**, 385 (1840). *Klassik. d. exakt. Wissen.* **9.**

This simple example will suffice to illustrate the application of the principle in thermochemistry. It is almost constantly used in dealing with the more complex reactions, especially in the field of organic chemistry. Indeed, without the aid of it, our knowledge of the thermochemistry of organic reactions would be very limited.

Hess made a second very important contribution to thermochemistry. When solutions of neutral salts are mixed there is no thermal change, and Hess expressed this fact in his *Law of the Thermoneutrality of Salt Solutions.* We shall see that this law is extremely interesting in the light of the theory of electrolytic dissociation, which furnishes for the first time a satisfactory explanation of it. Indeed, we shall learn how the law is a necessary consequence of this theory.

Hess attempted to explain the law of the thermo-neutrality of salt solutions, on the assumption that the heat evolved in salt formation depends only on the nature of the acid and not at all on the nature of the base. This assumption was erroneous and, therefore, the explanation based upon it.

So important is the work of Hess that he is regarded as the father of all modern thermochemistry.

Work of Favre and Silbermann. — The experimental work of Favre and Silbermann[1] is of the very greatest importance for the development of thermochemistry. There are few physical measurements more difficult than the determination of the amount of heat. The determination of temperature alone is not always a simple matter, but this is but the first stage in determining the quantity of heat. To determine the amount of heat, we must allow this to warm some substance like water, and must know the rise in temperature produced and the amount of water used. The experimental solution to a thermochemical problem, therefore, involves several steps. When the heat is liberated in the reaction, it must be taken up by some substance whose specific heat is known — say water.

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[1] *Ann. Chim. Phys.* [3], **34**, 357 ; **36**, 1 ; **37**, 406 (1852–1853).

The water must be enclosed in some form of vessel, and this vessel has a different specific heat from that of the water. Further, the vessel and water, as quickly as they become warmed above the temperature of surrounding objects, begin to radiate heat outward upon the colder objects. There is thus a continual loss of heat taking place during the experiment. Again, the liquid must be kept stirred during the experiment to secure uniform temperature throughout. The stirring produces heat, and the stirrer has a different specific heat from that of the water. The specific heat of the water itself must be determined at different temperatures, etc. These are just a few of a very large number of factors which have to be reckoned with in all thermochemical measurements.

The work of Favre and Silbermann had to do chiefly with the improvement of the experimental method for making calorimetric measurements. They devised a form of calorimeter which lies at the basis of all the forms which have been used since their time. They made a large number of thermochemical measurements, and showed that the heat of neutralization depends, not only on the acid as Hess had supposed, and not only on the base as Andrews[1] thought, but that it depends upon both. The investigations of Favre and Silbermann are nearly as important experimentally as those of Hess are theoretically for the development of modern thermochemistry.

Investigations of Julius Thomsen. — Thermochemistry in recent times has centred around two men; and our most reliable results were obtained by these men and their pupils. One of these is Julius Thomsen in Copenhagen. Thomsen's investigations[2] extend from the fifties up to the present. His collected works,[3] published in four volumes, contain the most important thermochemical data on record.

Thomsen recognized that all chemical reactions are accompanied by thermal changes, and undertook to measure the magnitude of these changes in a very large number of cases. He improved thermochemical methods far beyond any of his predecessors, and the methods which he employed have been subsequently improved only in certain minor points. The work of Thomsen will constantly reappear throughout the entire chapter on thermochemistry.

Berthelot's Investigations and Deductions. — It was stated that in recent times two men have led the work in thermochemistry. The one, a Dane, has just been mentioned; the work of the other, a Frenchman, — Berthelot, — will now be considered. The work of

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[1] *Pogg. Ann.* **54**, 208; **59**, 428; **66**, 31 (1841–1845).

[2] *Ibid.* **88**, 349 (1853); **90**, 261; **91**, 83 (1854); **92**, 34 (1853).

[3] *Thermochemische Untersuchungen.* 4 volumes (1882).

Berthelot was begun somewhat later than that of Thomsen; his first publication having appeared in 1865.[1] It was not until considerably later[2] that Berthelot began his experimental work, which has continued with more or less regularity up to the present. Berthelot improved a number of forms of apparatus, and devised new methods of work, which greatly extended our knowledge in this field. The Berthelot bomb, in which combustions were effected in oxygen under high pressure, made it possible to study, thermochemically, a large number of heats of combustion of organic substances, which could not have been dealt with under ordinary conditions. The work of Berthelot, like that of Thomsen, will constantly appear throughout this chapter. The three fundamental principles or generalizations at which he arrived should, however, be mentioned in this place.

I. The thermal change in a chemical reaction, if no external work is done, depends only on the condition of the system at the beginning and end of the reaction, and not on the intermediate conditions.

II. The heat evolved in a chemical process is a measure of the corresponding chemical and physical work.

III. "Every chemical transformation which takes place without the addition of energy from without, tends to form that substance or system of substances, the production of which is accompanied by the evolution of the maximum amount of heat."[3]

This third principle, which has come to be known as the law of maximum work, but which should be known as the law of maximum heat evolution, has also been stated by Berthelot[4] as follows:—

"Every chemical change which is accomplished without a preliminary action, or the addition of external energy, necessarily occurs if it is accompanied by disengagement of heat."

The third principle when stated in this form is known as the "principle of the necessity of reactions." We shall learn that the third principle of Berthelot is far from a rigid generalization. It holds in a large majority of cases, but there are so many exceptions known that it cannot be regarded as a law of nature. However, when we consider the vast number of cases to which the principle does apply, we see in it the germ of some great truth, which has not yet been fully understood and expressed.

With this preliminary historical introduction, we shall turn to the subject of thermochemistry proper.

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[1] *Ann. Chim. Phys.* [4], **6**, 290 (1865).

[2] *Ibid.* [4], **28**, 94 (1873).

[3] *Méc. Chim.* I, 29.

[4] *Loc. cit.*

CONSERVATION OF ENERGY APPLIED TO THERMOCHEMISTRY

Mass unchanged in Chemical Reactions. — One of the facts fundamental to the whole science of chemistry is the conservation of mass. When chemical reaction takes place, the substances change most of their properties. A liquid may become a gas or a solid, a solid a liquid or a gas. A poisonous substance like chlorine may combine with a metal like sodium, forming a compound which is not only not injurious to the body, but nutritious; and so on through the entire list of properties except that of mass. Some of the most accurate experimental work which has ever been carried out had for its object the solution of the problem — is mass unchanged in chemical action? The epoch-making work of Stas on the atomic weights of some of the elements showed very slight differences between the sum of the masses of the products of a reaction, and the sum of the masses of the constituents which enter into the reaction. In no case, however, were these differences larger than the possible experimental errors.

In recent time, as we have already seen (p. 2), an investigation was carried out by Landolt[1] to determine whether the weight of the products of a reaction is exactly equal to the weight of the constituents before the reaction — weight being our means of measuring mass. The result showed that slight differences existed between the weight of the products of a reaction, and the weight of the constituents before the reaction; but these differences were always so small that no final conclusion could be drawn from them.

The conservation of mass, then, stands out as the one property of matter which always remains unchanged, regardless of the number and kind of chemical transformations through which the matter is passed. The importance of this great law of nature for the science of chemistry it is absolutely impossible to overestimate. If there was a change in mass in chemical reaction, all quantitative work would be impossible, and chemistry would be reduced to mere qualitative observations. The science of chemistry rests, fundamentally, upon the law of the conservation of mass. Another law of equal importance we shall now consider.

Energy unchanged in Chemical Reactions. — In chemical reactions two great changes take place.

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[1] *Ztschr. phys. Chem.* **12**, 1 (1893).

1. A change in all the properties of the substances which re except mass.

2. A change in the form of energy in the reacting substances.

While the form of energy changes, the question arises, is th any loss or gain in energy in chemical reactions? The law of conservation of energy, which is one of our best established laws nature, comes to our aid. This law is stated by Maxwell[1] as lows: "The total energy of any material system is a quantity wh can neither be increased nor diminished by any action between parts of the system, though it may be transformed into any of forms of which energy is susceptible."

The total energy is, then, the same after the reaction as bef Before the reaction the total energy was in the form of chemical or trinsic energy. After the reaction a part still remains in the f of intrinsic energy, a part is transformed into heat, and if there i change in volume, as almost always occurs, a part is spent in do external work.

If we represent the change in the intrinsic energy by dE, the h evolved or absorbed by $d\theta$, and the external work done by dW, have —

$$dE = d\vartheta + dW.$$

The law of the conservation of energy is as fundamental to science of thermochemistry as the law of the conservation of m is to the science of pure chemistry. If energy were either create destroyed in chemical reactions, we could, it is true, measure amount of heat liberated in chemical reactions; but such measu ments would have relatively little value; indeed, about the sa value as quantitative determinations in pure chemistry if the law the conservation of mass did not apply. The law of the conser tion of energy, which is the first principle of thermodynamics, then, the foundation of the science of thermochemistry.

Same Amount of Heat liberated under the Same Conditions. — same chemical reaction under the same conditions always libera the same amount of heat. In order to obtain this result the react must take place under exactly the same conditions. Thus, the h liberated when a given quantity of metal, say zinc, dissolves i certain solution of an acid, is a constant. But in order that amount of heat may be obtained, the metal and acid must be a definite temperature, and the solution of the acid must have a tain definite concentration. If the acid varies in concentration, products formed may be different, and, consequently, a different amount of intrinsic energy may be converted into heat. Again, we may have what is apparently the same chemical reaction taking place under different conditions, and giving rise to very different amounts of heat. Take, for example, the solution of zinc in sulphuric acid. When a given weight of zinc is dissolved in sulphuric acid of a certain concentration, a definite amount of heat is liberated. If the zinc is connected with some other element so as to form a battery, and then allowed to dissolve in sulphuric acid of the same concentration, a very different amount of heat will be liberated. The change in intrinsic energy, dE, is the same, but in the second case a part has been converted into electrical energy, and, therefore, the amount which remains to be converted into heat is less.

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[1] *Matter and Motion*, art. 74.

If we represent the second condition in terms of the general energy equation, we must introduce another term for the electrical energy into which a part of the intrinsic energy has been transformed. Let us call this dE_e. We should then have —

$$dE = d\vartheta + dE_e + dW.$$

The difference between the intrinsic energy of two systems is equal to the heat liberated, plus the electrical energy, plus the work done.

Importance of Thermochemical Measurements. — The importance of thermochemical measurements will appear at once from what has preceded. We have no means of measuring directly the intrinsic energy contained in a substance. The best we can do is to measure the difference in intrinsic energy between a system and another system into which this can be transformed. The best method of measuring this difference is to transform the one system into the other by chemical means, when the excess of the intrinsic energy in the one over that in the other will be transformed into heat; and if there is a change in volume, also into work. By measuring the amount of heat set free, and the external work done, we know at once the difference between the intrinsic energies of the two systems. Unless there is a gas formed or used up in the reaction, the external work done is very small, and can usually be neglected. The heat liberated is, then, a measure of the difference between the intrinsic energies of the substances which react, and the intrinsic energy of the products of the reaction. Thus, the heat liberated is a measure of the difference between the intrinsic energy of hydrogen plus that of chlorine, and the intrinsic energy of the hydrochloric acid formed.

Thermochemical measurements, then, are our best means, and in many cases our only means, of determining the difference between the intrinsic energies of two systems, one of which can be transformed into the other. This alone should suffice to show the importance of such work.

The "Heat Tone" of a Reaction. — The term "heat tone" of a reaction is so frequently used that it should be clearly explained in this connection. The *heat tone* of a reaction is the sum of the heat developed in the reaction and the external work expressed as heat which is done. Since we have reactions which evolve heat and are termed *exothermic*, and also reactions in which heat is absorbed and are termed *endothermic*, the heat tone may be positive or negative. The work done may be positive as when a gas is formed, or it may be negative as when a gas is used up; so that both of the factors of heat tone may be positive, or both may be negative, or one positive and the other negative. Since the heat evolved is so large with respect to the work done, the sign of this factor essentially conditions the sign of the heat tone.

THERMOCHEMICAL METHODS

The problem in thermochemical measurements is to determine the *amount* of heat which is liberated in chemical reactions. In order to do this the heat which is set free is allowed to warm a known quantity of some liquid whose specific heat is known. The rise in temperature is then measured by means of an accurate thermometer. The liquid which is best adapted to such work is water, and the water calorimeter is almost exclusively used at present.

The Water Calorimeter. — In all forms of the water calorimeter the heat which is liberated in the reaction is taken up by a known quantity of water. The reaction must, therefore, take place in some vessel surrounded by the water of the calorimeter. A platinum vessel is usually employed, holding from one-half to one litre. This is surrounded by a known quantity of water, which is placed in an outer vessel of silver or some other metal. This outer vessel is then surrounded by poorly conducting material so as to diminish the loss of heat by radiation. The substances which are to react either in the pure state or in solution are brought to the same temperature and then introduced into the innermost vessel. The temperature of the water is determined before and after the reaction, and from the rise in temperature, the quantity of water present, and its specific heat, the amount of heat liberated in the reaction is determined at once. A great many forms have been given to the water calorimeter for special purposes. The most important of the early forms, as has already been stated, was that devised by Favre and Silbermann.[1] For a number of modifications consult the works of Berthelot[2] and Thomsen.[3] One form will be described in some detail below, just to give a clear idea of the instrument as used in practice.

The form chosen is one which was designed and used by Berthelot[4] especially for reactions in solution, such as the neutralization of acids and bases. (The apparatus is shown in Fig. 34.) The platinum vessel *A*, holding about 600 c.c., is surrounded by a vessel of thin copper, which, in turn, is closely surrounded by a silver vessel *B*. The whole is introduced into a double-walled vessel of sheet iron *C* containing water between the walls. This water is agitated by means of the stirrer *D*, and its temperature read on the

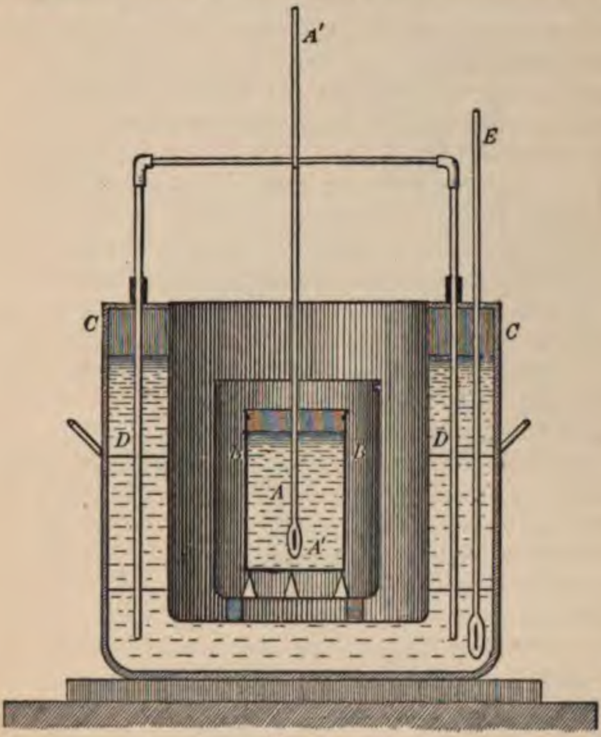

Fig. 34.

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[1] *Ann. Chim. Phys.* [3], **34**, 357 (1852) ; [3] **36**, 1 (1852).

[2] *Essai de Mécanique Chimique.*

[3] *Thermochemische Untersuchungen.*

[4] *Essai de Mécanique Chimique*, I, p. 140.

thermometer *E*. The whole apparatus is then surrounded by some non-conducting material, such as felt, and is kept in a room as nearly as possible at constant temperature.

If the liquids are such as would react on platinum, the innermost vessel should be made of very hard glass.

The liquid in the calorimeter proper (*A*) is stirred thoroughly by means of a platinum or glass stirrer, which is moved backward and forward in the liquid.

The thermometers employed must, of course, be very carefully calibrated and standardized against some standard instrument.

The Explosion Bomb. — In order that a reaction can be studied thermochemically, it must fulfil the following conditions: First, it must take place at ordinary temperatures; second, it must proceed rapidly to the end. A large number of reactions, which, under ordinary circumstances, do not fulfil the above conditions, can be made to fulfil them. Thus, many processes of combustion do not take place at ordinary temperatures at all in the air, and even at elevated temperatures require considerable time for their completion. Many such reactions can, however, be made to proceed rapidly to the end in a very brief period of time, if they take place in the presence of oxygen under increased pressure. For this purpose, an apparatus has been devised in which combustions can readily be effected at ordinary temperatures.

The combustion or explosion bomb, as it is termed, while bearing certain relations to a form of apparatus early devised by Andrews,[1] we really owe to Berthelot.[2]

The form of bomb which is used at present is seen in the accompanying figure (Fig. 35).

This is the form with which so much good work has been done by Stohmann[3] and his assistants in Leipzig; Stohmann himself having worked with Berthelot in Paris.

The walls of the bomb are of steel, and are sufficiently thick to withstand very great pressure. The bomb was lined on the inside with platinum. But since this required more than a thousand grams of platinum, it is obvious that some cheaper material would be very desirable. The lining used by Stohmann is enamel, which is not acted upon by many chemical substances. Upon the vessel *b*, is placed a weighed amount of the substance whose heat of combustion is to be determined. An iron wire of known length rests upon the substance, and through this wire an electric current can be passed. The iron burns readily in the oxygen when once heated by the current, and ignites the substance. The bomb is filled with oxygen under a pressure of about 25 atmospheres, from a cylinder containing oxygen under a higher pressure, and then closed by tightly screwing down the top. The whole bomb is then immersed in the water of a suitably arranged calorimeter. The current is passed through the wire, which burns in the oxygen and ignites the substance; and the combustion of the tablet of the substance is quickly completed. The heat liberated is measured in the water calorimeter in the usual manner.

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[1] *Pogg. Ann.* **75**, 27 (1848).

[2] *Ann. Chim. Phys.* [5], **23**, 160 (1881); [6], **10**, 433 (1887).

[3] *Journ. prakt. Chem.* **39**, 503 (1889).

A large number of corrections have to be introduced into all such measurements. Thus, the heat which is liberated when the iron wire burns, must be taken into account. Further, the bomb is filled with air at the outset, and the nitrogen of this air is oxidized to nitric acid. This reaction liberates heat, and the amount must be ascertained and the correction applied.

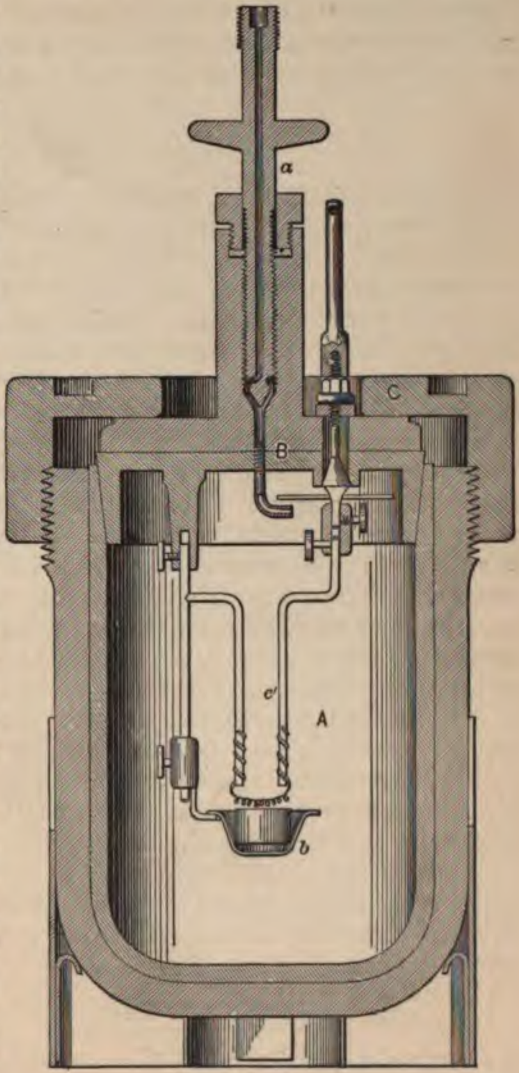

Fig. 35.

In addition, there are all the ordinary corrections of calorimetry, and many further details which must be learned by practice with the apparatus.

By means of this apparatus the heats of combustion of a large number of substances have been studied, and our thermochemical knowledge greatly extended in the field of organic chemistry.

THERMOCHEMICAL UNITS AND SYMBOLS

Units used in Thermochemistry. — The unit of heat in thermochemical measurements is the calorie. The calorie has been defined as the quantity of heat required to raise one cubic centimetre of water one degree in temperature. This definition would be exact if it had not been shown that the specific heat of water varies with the temperature. The work of Rowland and others has made it certain that the amount of heat required to raise the temperature of 1 c.c. of water from 0° to 1°, is not the same as the amount necessary to raise the temperature of the same quantity of water from 20° to 21°, or from 50° to 51°. In our definition of calorie we must, therefore, specify the temperature; and the temperature usually chosen is the ordinary temperature, 16° to 18°. The difference of a degree is not a matter of any very great importance, since the specific heat of water changes very slightly over this range in temperature.

It has also been suggested that we define a calorie as $\frac{1}{100}$ of the amount of heat required to raise 1 c.c. of water from 0° to 100°, and the suggestion is undoubtedly valuable.

The calorie most frequently used in thermochemical measurements refers to 18°, and it is in terms of this unit that thermochemical results are usually expressed. It is written "cal."

Ostwald has suggested a larger unit which is one hundred times the smaller, and is written K. $K = 100$ cal.

There is also a still larger unit which is frequently used, and which is one thousand times the smallest unit. It is written "Cal." We have, then, the following relations between the three units: —

$$K = 100 \text{ cals.};$$
$$\text{Cal} = 10 \text{ K} = 1000 \text{ cals.}$$

Thermochemical Symbols. — The methods of expressing the results of thermochemical measurements are simple. The symbols of the substances which react mean gram-atomic weights of the substances. Thus —

$$H_2 + O = H_2O + 68{,}360 \text{ cals.}$$

means that when 2 g. of hydrogen unite with 16 g. of oxygen, forming 18 g. of water at ordinary temperatures, there are 68,360 calories of heat liberated. These same facts are sometimes expressed thus: —

$$[H_2, O] = 68{,}360 +.$$

The plus sign means that heat is liberated or that the reaction is exothermic. A minus sign would mean that the reaction is endothermic, or that heat is absorbed.

If we interpret this in terms of our energy conceptions, it means that the intrinsic energy of 2 g. of hydrogen, plus the intrinsic energy of 16 g. of oxygen, exceed the intrinsic energy of 18 g. of water by 68,360 calories.

The same principle holds when compounds react. Thus —

$$NH_3 + HCl = NH_4Cl + 41{,}900 \text{ cals.}$$

means that when 36.45 g. of hydrochloric acid combine with 17.07 g. of ammonia, 41,900 calories of heat are liberated. This is also written: —

$$[NH_3, HCl] = 41{,}900.$$

If we wish to represent that the reaction takes place in solution, the presence of the large quantity of water is represented by the symbol aq. Thus —

$$KOH \text{ aq} + HCl \text{ aq} = KCl \text{ aq} + 13{,}700 \text{ cals.}$$

means that when a gram-molecular weight of caustic potash in solution in water reacts with a gram-molecular weight of hydrochloric acid in aqueous solution, there is formed a gram-molecular weight of potassium chloride in aqueous solution, and 13,700 calories of heat are liberated.

If we wish to represent the heat set free when a substance dissolves in water, the symbol aq is written after the formula of the substance: $HCl, aq = 17{,}320$ means that 17,320 calories of heat are liberated when a gram-molecular weight of hydrochloric acid gas is dissolved in water.

If we wish to represent both chemical action and solution, we write as follows: —

$$H + Cl + aq = HCl + aq + 39{,}300 \text{ cals.}$$

And this means that when 1 g. of hydrogen combines with 35.4 g. of chlorine in the presence of water which absorbs the hydrochloric acid formed, the heat set free due to combination and solution is 39,300 calories.

If a compound is broken down into its constituents, this fact is expressed by placing the minus sign before the formula of the substance: —

$$-\mathrm{HCl} = -22{,}000 \text{ cals.}$$

And this means that when a gram-molecular weight of hydrochloric acid is decomposed into hydrogen and chlorine, 22,000 calories of heat are absorbed.

If we wish to represent the state of aggregation of the substances which react and the products formed, this can be done as follows: The gaseous condition is represented by italics, the liquid by ordinary type, and the solid by extra heavy type.

$$H_2O = \text{water-vapor};$$
$$\mathrm{H_2O} = \text{liquid water};$$
$$\mathbf{H_2O} = \text{ice}.$$
$$H_2O_{100^\circ} - \mathrm{H_2O}_{100^\circ} = 9670 \text{ cals.}$$

This means that when a gram-molecular weight of water-vapor at 100° is condensed to water at 100°, so many calories of heat are set free. The application to other cases is self-evident.

SOME RESULTS WITH THE ELEMENTS

It would be impossible within the scope of this work to give an account of any considerable proportion of the thermochemical results which have been obtained. A few of the more interesting results with certain elements and compounds will, however, be very briefly referred to. We shall take up first some rather striking results which were secured with certain elements.

Oxygen. — Oxygen is known to exist in two modifications, — ordinary oxygen and ozone. The difference between these two is usually referred to the number of atoms contained in the molecule, — oxygen containing two atoms, ozone three.

The chemical properties of these two forms of oxygen are very different, ozone being the more active chemically. This would lead us to suspect that the molecule of ozone contains more energy than the molecule of oxygen. This has been tested by thermochemical methods. Hollmann burned the same substance in oxygen and in ozone. The end products were the same in both cases. Therefore, any difference in the amounts of heat liberated must have been the thermal equivalent of the excess of intrinsic energy in the one form of oxygen over that in the other. He found that more heat was liberated when the substance was burned in ozone, and concluded that the difference in intrinsic energy of the two modifications of oxygen was to be expressed by the following equation: —

$$2\,O_3 = 3\,O_2 + 2 \times 17{,}100 \text{ cals.}$$

More recent determinations have shown larger differences between the intrinsic energies of the two modifications of oxygen. Thus, Berthelot[1] oxidized arsenious to arsenic acid, on the one hand by oxygen, on the other by ozone, and concluded from the results that —

$$2\,O_3 = 3\,O_2 + 2 \times 29{,}600 \text{ cals.}$$

The still more recent work of Van der Meulen, in which ozone was decomposed by platinum black, gave the result —

$$2\,O_3 = 3\,O_2 + 2 \times 36{,}200 \text{ cals.}$$

These results show conclusively that a difference exists between the intrinsic energy of the molecule of oxygen and that of ozone, and that the molecule of ozone contains the greater amount of energy. The differences in the chemical properties of these two modifications of oxygen is, undoubtedly, very closely associated with this difference in the amounts of energy stored up in their molecules. We shall see that similar relations exist with other elements which occur in more than one modification.

Sulphur. — Sulphur exists in two crystalline modifications. The more common form is orthorhombic, and is obtained when ordinary amorphous sulphur is dissolved in carbon bisulphide and the solution evaporated. When, on the other hand, ordinary sulphur is melted and allowed to cool rapidly, we obtain monoclinic crystals. The monoclinic form is much less stable than the orthorhombic at ordinary temperatures, and readily passes over into the latter. It, therefore, seems to be the analogue of ozone, and orthorhombic sulphur of ordinary oxygen, since ozone readily passes over into ordinary oxygen. We should, then, expect that the molecule of monoclinic sulphur would contain more intrinsic energy than that of orthorhombic sulphur. This was tested by Favre and Silbermann.[2] When orthorhombic sulphur was burned, 71,000 calories of heat were liberated. When monoclinic sulphur was burned, 73,300 calories were set free. The difference, 2300 calories, is the thermal equivalent of the difference in the intrinsic energy of the two modifications.

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[1] *Ann. Chim. Phys.* [5], **10**, 162 (1876).

[2] *Ibid.* [3], **34**, 443 (1852).

Carbon. — Carbon exists in a number of modifications, — ordinary amorphous carbon, graphite, diamond, etc. The same question arises here as has already been considered in the cases of oxygen and sulphur: is there a different amount of energy contained in the molecules of these different forms of carbon? This has been answered by Favre and Silbermann,[1] who determined the heats of combustion of the different modifications of carbon, and found: —

For charcoal	96,980 cals.
For retort carbon	96,530 cals.
For graphite	93,360 cals.
For diamond	93,240 cals. 94,550 cals.

Of the different modifications of carbon, charcoal contains the greatest amount of energy, and the crystallized modifications, graphite and diamond, the least. The same general results obtained with other elements appear here in the case of carbon.

Phosphorus. — A fourth non-metallic element which exists in more than one form is phosphorus — yellow or ordinary phosphorus and the red modification. These contain different amounts of energy in their molecules, as is shown by the different amounts of heat set free when they are burned to the same end product. When yellow phosphorus is transformed into red there are about 27,300 calories of heat liberated. This is approximately the thermal equivalent of the difference between the intrinsic energies of the two modifications.

Much work has been done on the thermochemistry of other inorganic elements, and also an enormous amount on the thermal relations of the metallic elements; but for the results obtained, reference must be had to some of the larger works,[2] which deal more in detail with thermochemical results.

NEUTRALIZATION OF ACIDS AND BASES

Heat of Neutralization. — When solutions of acids and bases are brought together, heat is liberated. Quantitative measurements of the amounts of heat set free, brought out a simple and very important relation. This can best be seen from the following results for strong acids and bases. Gram-molecular weights of different acids were brought together with a gram-molecular weight of a given base, both the acid and base being present in very dilute solution. The amounts of heat set free by a number of acids when neutralized with the base sodium hydroxide, were:—

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[1] *Ann. Chim. Phys.* [3], **34**, 408 (1852).

[2] Ostwald: *Lehrb. d. Allg. Chem.* II. Thomsen: *Thermochemische Untersuchungen.* Berthelot: *Essai de Mécanique Chimique.*

	HEAT OF NEUTRALIZATION
Hydrochloric acid and sodium hydroxide	13,700 cals.
Hydrobromic acid and sodium hydroxide	13,700 cals.
Nitric acid and sodium hydroxide	13,700 cals.
Hydriodic acid and sodium hydroxide	13,800 cals.
Chloric acid and sodium hydroxide	13,760 cals.
Bromic acid and sodium hydroxide	13,780 cals.
Iodic acid and sodium hydroxide	13,810 cals.

The remarkable fact comes out that the heat of neutralization of these strong acids with a given base, sodium hydroxide, is a constant.

This suggests a further question very closely correlated to the above. Suppose we neutralize a given acid with a number of bases, will the heat liberated be a constant, and if so, will this bear any close relation to the above constant where the base was the same and the acid changed? This can be answered by the following results, in which hydrochloric acid was neutralized by a number of bases:—

	HEAT OF NEUTRALIZATION
Hydrochloric acid and lithium hydroxide	13,700 cals.
Hydrochloric acid and potassium hydroxide	13,700 cals.
Hydrochloric acid and barium hydroxide	13,800 cals.
Hydrochloric acid and calcium hydroxide	13,900 cals.

The heat of neutralization of a given acid with a number of bases is also a constant, provided the acid and bases are present in very dilute solution. But what is even more surprising, the constant in this case has the same value as in the preceding case where the base was unchanged, and the nature of the acid varied.

These facts when they were first discovered were very perplexing. Indeed, no satisfactory explanation of them could be furnished, and it was not until the theory of electrolytic dissociation was proposed that we could account for them at all.

Explanation of the Constant Heat of Neutralization of Strong Acids and Strong Bases.—It is one of the crowning glories of the theory of electrolytic dissociation, that it not only explains all of the facts in connection with the neutralization of strong acids and bases in dilute aqueous solution; but these facts are a necessary consequence of the theory.

Take, as an example, hydrochloric acid and sodium hydroxide. In a very dilute aqueous solution of hydrochloric acid all the molecules are dissociated into hydrogen and chlorine ions thus:—

$$HCl = \overset{+}{H} + \overset{-}{Cl}.$$

Similarly, in dilute aqueous solution, the molecules of sodium hydroxide are completely broken down into ions: —

$$NaOH = \overset{+}{Na} + \overset{-}{O}H.$$

When the dilute aqueous solutions of the base and acid are brought together, the following reaction takes place: —

$$\overset{+}{Na} + \overset{-}{O}H + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{Na} + \overset{-}{Cl} + H_2O.$$

The cation of the base-sodium, and the anion of the acid-chlorine, remain in solution as ions after the process of neutralization in exactly the same condition as before neutralization took place. The anion of the base-hydroxyl and the cation of the acid-hydrogen combine and form a molecule of water.

It may be urged that the sodium and chlorine ions combine, since sodium chloride is formed as the result of the neutralization. The salt is formed if the solution is evaporated; *i.e.* if the solution is concentrated. But it can be shown by several separate and independent methods, that a dilute solution of sodium chloride contains only ions and no molecules. The sodium and chlorine, then, remain as ions.

The hydrogen and hydroxyl combine and form a molecule of water. This is proved by the fact that water is always formed as the result of the process of neutralization; and further, it has been shown by a half-dozen different methods[1] that hydrogen and hydroxyl ions cannot remain in the presence of one another uncombined to any appreciable extent. This is the same as to say that water is practically undissociated.

Since hydroxyl is the anion of every base, and hydrogen the cation of every acid, the process of neutralization of any strong acid with any strong base in dilute solution, consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid, forming a molecule of water.

The process of neutralization of any acid by any base is, therefore, exactly the same as the process of neutralization of any other acid by any other base. The total heat that is liberated when a gram-equivalent of a completely dissociated acid acts on a gram-equivalent of a completely dissociated base, is the heat set free by the union of a gram-equivalent of hydroxyl ions with a gram-equivalent of hydrogen ions. Thus: —

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[1] Ostwald: *Ztschr. phys. Chem.* **11**, 521 (1893). Wijs: *Ibid.* **11**, 492; **12**, 514 (1893). Arrhenius: *Ibid.* **11**, 827 (1893). Bredig: *Ibid.* **11**, 830 (1893). Nernst: *Ibid.* **14**, 155 (1894). Kohlrausch and Heydweiller: *Ibid.* **14**, 317 (1894).

$$\overset{+}{H}\,aq + \overset{-}{O}H\,aq = 13{,}700 \text{ cals.}$$

Since all processes of neutralization of completely dissociated acids and bases are the same, the heat of neutralization of all such acids and bases must be a constant, and must be the heat of combination of a gram-equivalent of hydroxyl and hydrogen ions.

Neutralization of Weak Acids and Bases. — If either the acid or base is what we term weak, the heat of neutralization is not 13,700 calories, but differs from this value. Thus, take the following examples: —

	HEAT OF NEUTRALIZATION
Formic acid and sodium hydroxide	13,400 cals.
Acetic acid and sodium hydroxide	13,300 cals.
Dichloracetic acid and sodium hydroxide . . .	14,830 cals.
Valeric acid and sodium hydroxide	14,000 cals.
Phosphoric acid and sodium hydroxide	14,830 cals.

In these cases the acids are weak and the base is strong; nevertheless, there are considerable differences between the heats of neutralization and the constant 13,700 calories.

Similar results were obtained when weak bases were neutralized with a strong acid. If, however, both acid and base are weak, the heat of neutralization differs still more from the constant 13,700 calories. A few examples of this condition are given below: —

	HEAT OF NEUTRALIZATION
Formic acid and ammonium hydroxide	11,900 cals.
Acetic acid and ammonium hydroxide	11,900 cals.
Valeric acid and ammonium hydroxide	12,700 cals.

When the weak base ammonia is neutralized by the weak organic acids, the heat of neutralization differs very widely from the constant 13,700.

Explanation of the Results with Weak Acids and Bases. — If the acid or base is weak, we shall learn that it is only little dissociated by water, even in dilute solutions. When only a part of the acid or base is dissociated, the process of neutralization could proceed only until all the dissociated substance had reacted; were it not for the fact that as soon as the ions already present begin to react, more ions would be formed from the undissociated molecules, or, in a word, the process of dissociation would continue as the reaction continued until all the molecules had dissociated.

When molecules dissociate into ions, heat is either evolved or consumed. The thermal change which accompanies the dissociation of the undissociated molecules, either increases or diminishes the amount of heat set free due to neutralization alone. If the heat of dissociation is positive, it adds itself to the heat of neutralization; if negative, it diminishes the heat of neutralization. Thus, the heat which is liberated when a weak acid acts on a weak base, may be either greater or less than the constant 13,700 calories — greater when the heat of dissociation is positive, less when it is negative. It could be equal to the constant only when the heat of dissociation is zero.

The facts, then, agree with the theory, not only when the acid and base are completely dissociated, but when the dissociation is not complete. We could predict from the theory of electrolytic dissociation that the heats of neutralization of weak acids and bases would not be a constant, with the same certainty that we could predict the constant value of the heats of neutralization of completely dissociated acids and bases. The apparent exceptions presented by the weak acids and bases furnish as strong confirmation of the theory as the cases which conform to rule.

Explanation of the Law of the Thermoneutrality of Solutions of Salts. — The theory of electrolytic dissociation furnishes us with the first rational explanation of the law of the thermoneutrality of salt solutions. This law, which it will be remembered was discovered by Hess, states that when dilute solutions of salts are mixed there is little or no change in the heat tone. This is a necessary consequence of our theory. Take two salts, sodium chloride and potassium bromide. In dilute aqueous solutions these exist entirely as ions: —

$$\mathrm{NaCl} = \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}};$$
$$\mathrm{KBr} = \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Br}}.$$

When the solutions of these salts are mixed, all of the parts remain in solution as ions. There is no chemical action whatsoever, every constituent remaining in the same condition after as before mixing. There is, then, absolutely no reason to expect any thermal change, and none results.

We can now begin to see the importance and wide-reaching significance of the theory of electrolytic dissociation. This theory furnishes us with the explanation of the constant heat of neutralization of acids and bases, and of the law of the thermoneutrality of salts; and this is but the beginning. We shall see as our subject develops, that it has thrown an entirely new light on a great number of chemical, physical, and biological problems which, without its aid, were simply empirically established facts, whose meaning was entirely shrouded in darkness. We shall see that this theory is fundamental, if we hope to raise chemistry from empiricism to the rank of an exact science.

Thermochemical Method of Determining the Relative Strengths of Acids and Bases. — One important application of the heat of neutralization must be considered here. We have seen that when a very dilute solution of any strong acid acts on a very dilute solution of any strong base, the heat liberated is a constant, independent of the nature of the acid and the nature of the base. This applies only to very dilute solutions. If the solutions are more concentrated, the heat liberated on neutralizing an acid with a base depends on the nature of the acid and also on the nature of the base. This fact has been utilized to determine the relative strength of acids and bases, and in the following way.

Given the problem to determine the relative strengths of hydrochloric and sulphuric acids. An equivalent of each acid is neutralized by an equivalent of some base, say sodium hydroxide; and the amount of heat set free in each case, determined.

To one equivalent of hydrochloric acid and one equivalent of sulphuric acid, under the same conditions as above, and in the presence of each other, one equivalent of the base is added. If all the base went to the hydrochloric acid, the heat liberated would be the same as that set free when the base acted on hydrochloric acid alone. If all the base went to the sulphuric acid, the heat liberated would be equal to the heat of neutralization of the sulphuric acid by the base, under the same conditions. If the base went part to the hydrochloric acid and part to the sulphuric, the amount of heat set free would lie between the above two values.

The latter condition is the one which always obtains. The amount of heat set free falls between the amounts liberated with each acid separately, and, consequently, a part of the base goes to each acid. Knowing the amount of heat liberated with each acid separately, and the amount of heat set free when the acids are treated in the presence of each other with one-half enough base to neutralize them, we know at once the way in which the acids divide the base between them; and this is the expression of the relative strengths of the acids.

The above line of reasoning is given for the sake of simplicity and clearness. In actual practice the mode of procedure is somewhat different, though the principle is the same. One acid is allowed to act on a salt of the other acid, and the final distribution of the base between the two acids determined by the amount of heat set free. This method of solving the problem is relatively complex. Take the action of nitric acid on, say, sodium sulphate. It is necessary to know the heat liberated when nitric acid is neutralized by the base, when sulphuric acid is neutralized by the base, the heat evolved when sulphuric acid acts on sodium sulphate, when nitric acid acts on sodium nitrate, and also whether there is heat evolved when the two acids are brought together.

Given all of the above data, it is possible to determine, approximately, the relative strengths of nitric and sulphuric acids. It is, however, obvious that this method of determining the strengths of acids is very complicated, and further, when we consider the relatively large errors in all thermochemical measurements, the results obtained in this way could not be more than approximations. The above method of determining the relative strengths of acids is not used at all at present, since, as we shall soon learn, we have far more accurate and very simple methods for solving such problems. The thermochemical method has been briefly considered here for the sake of completeness, and because it acquired considerable prominence at a somewhat earlier period.

The thermochemical method of determining the relative strength of bases is exactly the same in principle as that described above for acids. Given two bases whose relative strengths are to be determined. An equivalent of each base is neutralized with a given acid, and the amount of heat measured. Then one equivalent of the acid is added to one equivalent of the two bases in the presence of each other, and the amount of heat determined. From the relations of these three quantities the division of the acid between the two bases is ascertained. Here, again, in practice one base is allowed to act on the salt of the other base with the acid, and the division of the acid between the two bases determined by thermal methods. The method here is just as complex as when applied to the relative strengths of acids, and has been entirely supplanted by more refined methods for determining the relative strengths of bases.

SOME RESULTS WITH ORGANIC COMPOUNDS

Heat of Formation. — By heat of formation of a compound we mean the amount of heat which is set free or absorbed when the compound is formed by a direct combination of the constituent elements. In order that the term "heat of formation" may have a quantitative significance, we must deal with definite amounts of substances; and in order that the heats of formation of different substances may be comparable, we must deal with comparable amounts of substances. We choose for sake of convenience gram-molecular weights of substances, and determine heats of formation in terms of these quantities. The heat of formation of a compound is, then, the amount of heat set free or absorbed when a gram-molecular weight of the compound is formed from its elements.

The heat of combination of a compound may be determined in many cases directly, by allowing the elements to combine and measuring the heat set free; but in many cases this is not possible. A large number of substances cannot be formed directly from the elements. In such cases an indirect method of determining the heat of formation must be employed. The indirect method most commonly used is to burn the elements in oxygen; then burn the compound in oxygen, and measure in each case the amount of heat set free. Since the products of the combustion of the elements are the same as the products of the combustion of the compound containing these elements, any difference in the amounts of heat set free in the two cases is the heat of formation of the compound.

Take the case of methane. It would be impossible to determine directly the heat of formation of methane. This can, however, be determined very easily by burning carbon in oxygen, by burning hydrogen in oxygen, and finally by burning the methane in oxygen. Any difference between the heat of combustion of the compound and the sum of the heats of combustion of the elements is the heat of formation of the compound. The following results were obtained in this case: —

Heat liberated by burning 12 g. C in oxygen	96,960 cals.
Heat liberated by burning 4 g. H in oxygen	136,720 cals.
	Sum = 233,680 cals.
Heat liberated by burning 16 g. methane in oxygen	211,930 cals.

The difference between the two values, 21,750 calories, is the heat of formation of methane.

In a manner exactly similar to the above, the heats of formation of a large number of compounds have been worked out. Indeed, there are comparatively few compounds formed directly from the elements with sufficient ease to enable their heats of formation to be measured directly. The above indirect method of measuring heat of formation is therefore applied in a large majority of cases.

Heat of Combustion. — By heat of combustion of a compound is meant the heat which is evolved when a compound is completely burned in oxygen. The carbon under these conditions is completely oxidized to carbon dioxide, the hydrogen to water, the nitrogen to nitric acid, and the sulphur to sulphur trioxide. The heat of combustion of organic compounds is a very important quantity to determine, since it is the only means, in many cases, of determining the heat of formation of the substance. As we have just seen, it is only necessary to determine the heat of combustion of the elements which enter into a compound, and the heat of combustion of the compound itself, and then to subtract the one from the other, in order to arrive at the heat of formation of the compound from its elements.

Indeed, the most important quantity by far in the field of organic chemistry, from the thermochemical standpoint, is the heat of combustion. In order that this should be determined, it is necessary that the combustion should proceed to the end at once, and that all the constituents should be completely oxidized. For this purpose the combustion bomb, which has been already described, was devised and used. In an atmosphere of relatively concentrated oxygen, *i.e.* oxygen under high pressure, most organic compounds are completely oxidized; and by means of the explosion method the heats of combustion of an enormous number of organic substances have been ascertained by Berthelot,[1] Thomsen,[2] Stohmann, and Langbein,[3] and others. A few of the more interesting of these results are given below.

Saturated or Methane Hydrocarbons. —The heats of combustion of a number of members of this series have been measured by Thomsen and others. The results for a few hydrocarbons are given below: —

HYDROCARBONS	HEAT OF COMBUSTION	DIFFERENCES
Methane, CH_4	211.9 Cals.	
		158.5 Cals.
Ethane, C_2H_6	370.4 Cals.	
		158.8 Cals.
Propane, C_3H_8	529.2 Cals.	
		158.0 Cals.
Butane, C_4H_{10}	687.2 Cals.	
		159.9 Cals.
Pentane, C_5H_{12}	847.1 Cals.	

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[1] *Essai de Mécanique Chimique.* [2] *Thermochemische Untersuchungen.*
[3] *Journ. prakt. Chem.* 1885–1895.

A constant difference in composition of CH_2 corresponds to very nearly a constant difference in the heat of combustion. This amounts to about 159 calories.

The effect of constitution in this series of hydrocarbons is practically zero, — a normal compound having the same heat of combustion as an isocompound of the same composition.

The Unsaturated (Ethylene and Acetylene) Hydrocarbons. — The results with the unsaturated hydrocarbons are very similar to those with the saturated.

Ethylene Hydrocarbons	Heat of Combustion	Difference
Ethylene, C_2H_4	333.4 Cals.	159.3 Cals.
Propylene, C_3H_6	492.7 Cals.	157.9 Cals.
Isobutylene, C_4H_8	650.6 Cals.	157.0 Cals.
Amylene, C_5H_{10}	807.6 Cals.	

Acetylene Hydrocarbons	Heat of Combustion	Difference
Acetylene, C_2H_2	310.1 Cals.	157.5 Cals.
Allylene, C_3H_4	467.6 Cals.	

The constant difference in composition of CH_2 has a constant influence on the heat of combustion, whether the compound contains a larger or smaller number of carbon atoms.

A fact brought out by the above results, of more than ordinary interest, is that the constant difference in composition of CH_2 produces the same difference in the heat of combustion, whether we are dealing with saturated hydrocarbons or with either of the series of unsaturated hydrocarbons. The meaning of this fact is not at present clear, but it is certainly important from the standpoint of the constitution of these substances.

Alcohols. — The alcohols differ from the corresponding hydrocarbons in that they contain one atom of oxygen more than the latter. They thus represent the first stage of oxidation of the hydrocarbons. The heat of combustion of the alcohols is less than that of the hydrocarbons, as we would expect, since they are already partly oxidized. A few results are given: —

ALCOHOLS	HEAT OF COMBUSTION	DIFFERENCE
Methyl alcohol, CH_4O	182.2 Cals.	158.3 Cals.
Ethyl alcohol, C_2H_6O	340.5 Cals.	158.1 Cals.
Propyl alcohol, C_3H_8O	498.6 Cals.	159.9 Cals.
Isobutyl alcohol, $C_4H_{10}O$	658.5 Cals.	

We observe the same relation here as with the hydrocarbons. A constant difference in composition between succeeding members of the homologous series corresponds to a constant difference in the heat of combustion.

As we have stated, the hydrocarbons differ from the corresponding alcohols in that the latter contain an oxygen atom. We should, therefore, expect a nearly constant difference between the heat of combustion of the hydrocarbon and the alcohol. Facts substantiate this conclusion.

Heat of combustion of $CH_4 - CH_4O = 29.7$ Cals.
Heat of combustion of $C_2H_6 - C_2H_6O = 29.9$ Cals.
Heat of combustion of $C_3H_8 - C_3H_8O = 30.6$ Cals.
Heat of combustion of $C_4H_{10} - C_4H_{10}O = 28.7$ Cals.

Results similar to the above were obtained with other oxidation products of the hydrocarbons. In some cases the effect of constitution was more pronounced than in others, but, on the whole, nothing essentially new would be brought out by going farther into details in this direction. One further class of paraffine derivatives must, however, be considered.

Halogen Substitution Products of the Paraffines. — Take first the chlorine derivatives of the paraffines. A constant difference in composition corresponds to a constant difference in the heat of combustion.

	HEAT OF COMBUSTION	DIFFERENCE
Methyl chloride, CH_3Cl	164.8 Cals.	157.1
Ethyl chloride, C_2H_5Cl	321.9 Cals.	158.3
Propyl chloride, C_3H_7Cl	480.2 Cals.	157.7
Isobutyl chloride, C_4H_9Cl	637.9 Cals.	

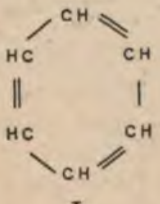
Results of a similar character were obtained with other halogen derivatives of the paraffines.

An interesting relation between the heats of formation of the chlorides, bromides, and iodides of the paraffines has been pointed out by Ostwald.[1] He gives the following table of results, calculated from the heats of combustion of the compounds and of the elements: —

	Heat of Formation		Heat of Formation	Diff.
CH_3Cl	22.0 Cals. > 7.4	CH_3Br	14.2 Cals.	7.8 Cals.
C_2H_5Cl	29.6 Cals.	C_2H_5Br	21.8 Cals.	7.8 Cals.
C_3H_7Cl	36.0 Cals. > 6.4	C_3H_7Br	29.1 Cals.	6.9 Cals.
		CH_3I	2.8 Cals.	19.2 Cals.
		C_2H_5I	9.9 Cals.	19.7 Cals.

There is a constant difference between the heats of formation of the bromides and chlorides, and the iodides and chlorides. This difference is independent of the size of the group combined with the halogen, *i.e.* whether it is methyl, ethyl, propyl, etc. Results of this kind are certainly very closely connected with the fundamental problems of the combination of matter.

The Thermochemistry of Benzene. — The thermochemical results which have been obtained with benzene are especially interesting, as showing a new application of the results of such measurements. The problem of the constitution of benzene has been, and is still, one of the fundamental problems of organic chemistry. The molecule contains six carbon atoms and six hydrogen atoms, and the fundamental question is the way in which the carbon atoms are united. The two possibilities between which it has been found difficult to decide are the following: —



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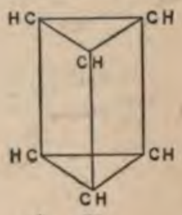

II

In I the carbon atoms are united alternately by single and double union. There are three double and three single bonds in the molecule. In II all the carbon atoms are united by single bonds. There are nine single bonds in the molecule. The first formula is the well-known hexagon of Kekulé; the second, the prism formula of Ladenburg. The attempt has been made to decide between these formulas by thermochemical methods. Thomsen found[1] that when carbon is united with carbon by double linkage ($C=C$) the heat of combustion is different from that of carbon united to carbon by single linkage ($C-C$). He worked out, approximately, the heat of combustion of carbon under these two conditions, and also the heat of combustion of six hydrogen atoms. He then determined the heat of combustion of benzene, and found the value 788 Cals. When the heat of combustion of the six hydrogen atoms was subtracted from this quantity, the remainder was found to correspond to the condition of six carbon atoms united by single union. In a word, there are nine single unions in benzene, or the prism formula of Ladenburg represents the structure of the benzene molecule.

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[1] *Lehrb. d. Allg. Chem.* II, p. 390.

We must not, however, accept this conclusion as in any way final. We have seen that exactly the opposite result was reached by Brühl from a study of the refractivity of benzene. He concluded from his work, that there are three single and three double bonds in the benzene molecule.

It must also be remembered that no one method is capable of settling such a problem, to the exclusion of the results of all other methods. A great many purely chemical methods have been brought to bear on the problem of the constitution of benzene, with the general result that the hexagonal formula of Kekulé seems to account for the facts rather better than any other which has been proposed. There is this objection, however, to the formula of Kekulé, that it represents the benzene molecule as occupying only two dimensions in space. It should be stated in this connection that a number of facts have been pointed out, especially by Ladenburg, which seem to indicate the general correctness of the prism formula. It is thus obvious that the question of the constitution of benzene is still an open one.

Effect of Constitution on Heat of Combustion. — Certain striking relations between the heats of combustion of compounds and their differences in composition have been pointed out. We must not, however, draw the conclusion that heat of combustion is conditioned only by the composition of the molecule. The constitution of the molecule, or the way in which its constituents are united, has a marked influence, in many cases other than benzene, on the heat of combustion. To determine the effect of constitution on heat of combustion, it is necessary to compare substances having the same composition, but different constitution. Such are, of course, the well-known isomeric compounds. If we compare isomeric compounds having nearly the same constitution, we shall find comparatively slight differences in the heats of combustion. This is shown by the following example: —

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[1] *Thermochemische Untersuchungen.*

	Heat of Combustion
Methyl acetate, CH_3COOCH_3	395 Cals.
Ethyl formate, $HCOOC_2H_5$	390 Cals.

If the isomeric compounds differ still more in constitution, the difference in the heats of combustion will be still greater. Take the compounds: —

	Heat of Combustion
Methyl formate, $HCOOCH_3$	252 Cals.
Acetic acid, CH_3COOH	210 Cals.

When the difference in constitution is very great, there may be a very large difference between the heats of combustion, as in the case given below: —

	Heat of Combustion
Benzene, C_6H_6	788.0 Cals.
Dipropargyl, C_6H_6	883.2 Cals.

No very important generalization connecting constitution and thermal relations has been reached. The data at hand are far too meagre, and the phenomena dealt with perhaps too complex, to admit at present of any wide-reaching conclusion. It is, however, quite clear from the above examples, that constitution has a marked influence on heat of combustion; and this is the point upon which it is desired to lay stress in this place.

The energy contained in a molecule is, then, not conditioned solely by the number and kind of atoms present, but also by the way in which they are combined with one another. This is proved by the fact that the heats of combustion of isomeric substances differ; and since the end products in such cases are the same, the molecules of isomeric substances must contain different amounts of energy.

CHAPTER VII

ELECTROCHEMISTRY

DEVELOPMENT OF ELECTROCHEMISTRY

Earlier Observations. — The discovery of simple electrical phenomena preceded, by a long time, the recognition of the relation between electricity and other manifestations of energy. It was not until about the middle of the eighteenth century that Beccaria[1] showed that metals like zinc could be obtained from their oxides by means of the electric spark. In this reaction the chemical attraction between the zinc and the oxygen was overcome by means of electricity, and it appeared probable that some relation existed between the two.

The observation of Van Marum that metal wires when heated by the current in an atmosphere of nitrogen were not converted into the oxide, as they were in the presence of oxygen, was of special importance as bearing upon the theory of combustion in vogue at that time. A burning body was supposed to give off a substance having negative weight, called phlogiston. What we now call an oxide was then termed a "calc." The calc differed from the metal in that it contained less phlogiston.

If this was the true explanation of combustion, then there was no reason why a heated metal should not form a calc in nitrogen as well as in oxygen, since neither of these gases took part in combustion. The fact that no calc was formed in the presence of nitrogen was a strong argument against the theory of phlogiston, as a satisfactory and sufficient explanation of the phenomenon of combustion.

Galvani's Discovery. — It was not until the last decade of the eighteenth century that the wife of Galvani discovered by accident that when the crural nerve in the hind leg of a frog was touched with a scalpel, it was thrown into contraction by an electric discharge in the room. Galvani's investigations in this field brought out the fact that when both muscle and nerve were connected with metallic conductors, especially when these were of different metals, the contractions could be produced without the presence of an electric discharge. He asked himself whence the source of this electricity, and concluded that it must exist in the animal body. This was the origin of his theory of "animal electricity."

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[1] *Geschichte Elek.* (Priestly), Berlin, 1772.

Volta's Discovery of the Primary Battery. — That strong contractions in the muscle were produced only when different metals were used, showed to Volta[1] the insufficiency of the explanation offered by Galvani to account for the source of the electricity. Volta[1] pointed out clearly that in order that such contractions should be produced it was necessary that two different metals, or conductors of the first class, should be brought in contact, and at the same time their opposite ends should be brought in contact, with a conductor of the second class. There were thus two possible sources of the electricity; either at the contact of the two different metals with each other, or at the contact of the metals with the conductors of the second class, *i.e.* the liquids present in the animal itself. He concluded that the chief source was at the contact of the two metallic surfaces. Volta thus distinguished between conductors of the first and second classes; placing in the first those substances which conduct like the metals, in the second those which conduct like aqueous solutions.

The Voltaic Pile. — The recognition of chemical action as the cause of galvanic action led to the construction of the voltaic pile. Volta constructed his pile of zinc and silver, placed alternately over one another, and moistened these with a salt solution held by some porous material. The strength of such a pile depended upon the number of couples. The discovery of the voltaic pile or battery marks an epoch in the development of electrochemistry. This placed in the hands of the investigator an unlimited supply of electricity, which made it possible to carry on systematic investigations which had hitherto been impossible. From this time electrochemistry developed by enormous strides — one important discovery quickly following another.

The Electrolysis of Water. — The source of the electricity in the voltaic pile being due to the chemical action in the couple, they had to do here with a clear case of the transformation of chemical energy into electrical. The next step which naturally would have been taken was to determine whether it was possible to effect chemical decomposition by means of the current from such a pile. This was done by Nicholson and Carlisle[1] at the beginning of the nineteenth century. By means of the current they decomposed water into oxygen and hydrogen, the gases being liberated on the two poles of their couples. This was an important step, since it showed clearly the transformation of electrical energy into chemical, and made it strongly probable that there is a close relation between the two.

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[1] *Phil. Trans.* 1793, I, p. 10. *Grens' Journ. d. Phys.* **3**, 479 (1796).

Work of Davy. — At this time Humphry Davy[2] began his epoch-making experiments with the electric pile, which finally resulted in the separation of the alkali metals from their oxides. The decomposition of these oxides directly by the current was strong evidence in favor of some close relation between chemical attraction and electrical attraction. As the result of his electrochemical studies he was led to the *electrochemical theory* which bears his name. According to this theory, the atoms of different substances acquire different electrical charges by contact, and these attract one another because of the different charges upon them. The differences between the charges may be so small that the attraction between them will not be sufficient to cause the atoms to leave their former positions, or they may be great enough to effect such a rearrangement. In the latter case, a chemical compound is formed.

The chemical attraction of atoms depends, then, only upon the electrical attraction between the opposite charges which have accumulated upon them, due to their contact with one another. A large number of atoms, each with a small attractive power, may overcome a greater attraction between a smaller number of atoms. This accounts for the effect of mass in chemical action, which we shall learn is very great indeed.

Electrolysis, according to this theory, consists in equalizing the charges upon the atoms. The negatively charged atom receives positive electricity from the positive pole, to which it is attracted and becomes electrically neutral. The positively charged atom is attracted to, and electrically neutralized at, the negative pole. The compound is thus necessarily broken down, since the force which held its constituents together no longer exists.

The Electrochemical Theory of Berzelius. — The theory of Davy never acquired any prominence, and soon gave place to that of Berzelius, which differed from it fundamentally. According to Davy an atom as such is electrically zero, and becomes charged positive or negative by contact with another atom, which takes a charge of the opposite sign. Berzelius[1] claimed that every atom is charged with both kinds of electricity. These exist upon the atom in polar arrangement, and the electrical nature of the atom depends upon which kind of electricity is present in excess. One kind is usually present in large excess, giving the atom a decidedly positive or negative character. One "pole" is usually much stronger than the other, so that the atom reacts as if it were "unipolar." Chemical attraction is but the electrical attraction of these oppositely charged atoms, and the intensity of the former is conditioned by the magnitude of the charges upon the atoms. A negatively charged atom is attracted to, and combines with, one carrying a positive charge. The magnitude of these opposite charges may not be the same, the compound formed being electrically positive or negative, depending upon which kind of electricity is present in excess. Two compounds, the one charged positive and the other negative, may thus in turn combine, forming a still more complex compound. In this way Berzelius was able to account for the more complex substances, such as the so-called double compounds.

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[1] *Nicholson's Journ.* **4**, 179 (1800).

[2] *Ibid.* **4**, 275, 326. *Gilb. Ann.* **7**, 114 (1801); **28**, 1, 161 (1808). *Bakerian Lect. Roy. Soc.* (1806).

Objections to the Theory of Berzelius. — The theory as put forward by Berzelius did not long enjoy freedom from adverse criticism. Indeed, it seemed to carry with it, of necessity, a questionable consequence. If chemical union is due to the electrical attraction of oppositely charged atoms, which come together and more or less equalize their charges, then, as soon as the equalization is effected, the cause for the union no longer exists, and the constituents of the compound must fall apart. As soon, however, as any decomposition took place, the products of the decomposition would again become oppositely charged, would, therefore, attract one another and reunite. There would thus result a continual decomposition and reunion, and a chemical compound would always seem to be in a state of unstable equilibrium.

The theory, however, was soon called upon to meet what was supposed to be a very serious objection. If chemical union depends only upon the electrical charges upon the atoms, then, the properties of the compound formed would be a function of the electrical charges upon the atoms in the compound. It was found to be possible to substitute the three hydrogen atoms in the methyl group of acetic acid by three chlorine atoms, without seriously changing the properties of the compound. Berzelius could not satisfactorily explain this fact. The three hydrogen atoms each carried a positive charge, while the three chlorine atoms each carried a negative charge. That three positive charges could be replaced in a compound by three negative charges, without fundamentally changing the nature of the compound, was, for a long time, an insuperable objection to the electrochemical theory of Berzelius. Indeed, this argument was regarded until very recently as practically overthrowing the theory.

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[1] *Gilb. Ann.* **27**, 270 (1807). *Afh. i Fysik. Kemi och Miner*, Stockholm, 1806.

Thomson overthrows this Objection. — The above objection to the theory of Berzelius persisted nearly to the end of the nineteenth century. It has, however, been recently removed by the work of J. J. Thomson,[1] which will be referred to in this place as it bears so directly upon a theory whose importance is now very great indeed. Thomson has shown experimentally that the same element may be charged now positive, now negative, depending upon conditions. He electrolyzed hydrogen gas,[2] and found that positive hydrogen went to one pole and negative to the other. The spectra of the hydrogen around the two poles was studied and found to be quite different. The molecule of hydrogen gas is, then, very probably made up of a positive and a negative hydrogen ion.

We must not, therefore, conclude that because hydrogen is sometimes positively charged it is always so. Thomson's own words in connection with the bearing of his work on the theory of Berzelius are given below: —

"In many organic compounds, atoms of an electropositive element hydrogen are replaced by atoms of an electronegative element chlorine, without altering the type of the compound. Thus, for example, we can replace the 4 hydrogen atoms in CH_4 by Cl atoms, getting, successively, the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. It seemed of interest to investigate what was the nature of the charge of electricity on the chlorine atoms in these compounds. The point is of some historical interest, as the possibility of substituting an electronegative element in a compound for an electropositive one, was one of the chief objections against the electrochemical theory of Berzelius. When the vapor of chloroform was placed in the tube, it was found that both the H and Cl lines were bright on the negative side of the plate, while they were absent from the positive side, and that any increase in the brightness of the H lines was accompanied by an increase in the brightness of those due to Cl. . . . The appearance of the H and Cl spectra on the same side of the plate was also observed in methylene chloride and in ethylene chloride. Even when all the H in CH_4 was replaced by Cl, as in carbon tetrachloride CCl_4, the Cl spectra still clung to the *negative* side of the plate.

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[1] *Nature*, **52**, 453 (1895).

[2] *Ibid.* **52**, 451 (1895).

"The same point was tested with $SiCl_4$, and the Cl spectra was brightest on the *negative* side of the plate.

"From these experiments it would appear that the Cl atoms, in the chlorine derivatives of methane, are charged with electricity of the same sign as the H atoms they displace."

This work leaves the classical argument against the theory of Berzelius without foundation, since the hydrogen atoms in acetic acid are replaced by chlorine atoms which carry the same kind of charge as the hydrogen which they replace. Therefore, the properties of trichloracetic acid should resemble closely those of acetic acid if the theory of Berzelius is true, and such is the fact.

The Law of Faraday. — The period immediately following the one just considered, from an electrochemical standpoint, was not very fertile until we come to the investigations of Faraday.[1] Upon these investigations it is difficult to lay too much stress. Faraday showed the identity of electricity from different sources, whether produced by friction or by chemical action. He also studied the relation between the amount of chemical decomposition effected by a current in passing through a conductor of the second class, and the amount of electricity which flowed through the conductor. He found that the two were proportional to one another, and from this announced the first part of his law: —

The amount of chemical decomposition effected by the passage of the current is proportional to the amount of electricity which flows through the conductor.

This is one of the few laws of nature which seems to hold rigidly under all known conditions. There is no well-established exception to this law.

Faraday determined also the amounts of different elements which are separated from their compounds, by passing the same current through solutions of these compounds. For example, the same current was passed through solutions of, say, copper sulphate, zinc chloride, and silver nitrate, and the amounts of copper, zinc, and silver deposited determined by weighing the electrodes before and after the experiment. A generalization of very wide significance was reached, which is the second part of the law of Faraday: *The amounts of the different elements which are separated by the same quantity of electricity bear the same relation to one another as the*

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[1] *Expr. Researches*, III, Ser. No. 373 (1832).

equivalents of these elements. The atoms of all univalent elements carry exactly the same quantity of electricity, of bivalent elements twice as much, of trivalent three times as much, and so on. In a word, all univalent atoms carry the same amount of electricity, and all polyvalent atoms a simple, rational, multiple of the amount carried by univalent atoms — the multiple being the valence of the atom.

After Faraday proposed his law, confusion arose between the terms "quantity of electricity" and "electrical energy," and some confusion might still exist if we are not careful to consider the wide difference which exists between the meaning of these terms. Electrical energy, like every other manifestation of energy, can be factored into a capacity factor and an intensity factor. The capacity factor of electrical energy is the quantity of electricity, the intensity factor the potential. These bear the following relation to electrical energy: —

capacity factor × intensity factor = electrical energy,
or quantity × potential = electrical energy.

The law of Faraday says that when equal quantities of electricity are passed through conductors of the second class, chemically equivalent quantities of the different elements are separated from their compounds. It says nothing whatever about the potential required to effect the decompositions, and, consequently, nothing about the electrical energy required in the different cases. Indeed, it is self-evident that this would be very different in different cases.

Electrolysis. — The power of the electric current to effect the decomposition of chemical compounds was brought into special prominence by the work of Faraday. The decomposition of compounds by the current, he termed *electrolysis.* Some of the most important advances which were made at this period are along the line which we are now considering. Theories were proposed to account for the facts then known, which we recognize at the present day as containing the essence of one of the widest reaching generalizations in modern chemical science.

When the two poles of a voltaic cell were immersed in acidulated water, hydrogen was liberated upon the one pole, and oxygen upon the other. Between the two poles there was a layer of water particles, which apparently underwent no decomposition. The question arose, Do the hydrogen and oxygen set free come from the same or from different particles of water? It was not a simple matter to decide this point. A superficial glance at what took place would probably leave the impression that they came from different particles of water; yet it might be true that the water molecules which underwent decomposition were those which were halfway between the poles, and that the hydrogen moved from this point in one direction, and the oxygen in the other. Humphry Davy undertook to decide this question experimentally. He placed each pole of a voltaic cell in a vessel containing water, and connected the two vessels by placing a finger of one hand in the one vessel, and a finger of the other hand in the other vessel. He insulated his body from the earth by standing on a rubber plate. The electrolysis took place, and the gases separated from the electrodes just as if the vessels had been connected directly.

According to Davy, in such an arrangement it is difficult to see how the hydrogen and oxygen liberated at the poles could come from the same molecule of water. It was, therefore, probable, that in the ordinary electrolysis of water, the hydrogen and oxygen came from different molecules of water.

Theory of Grotthuss. — The first to account at all satisfactorily for electrolysis was Grotthuss,[1] at the early date of 1805. At the moment when the hydrogen and oxygen separate, the one becomes positive and the other negative. The positively charged hydrogen is attracted to the negative pole and repelled from the positive pole. The negatively charged oxygen is attracted to the positive and repelled from the negative pole. This clear and concise idea of Grotthuss is represented graphically in the accompanying figure (36).

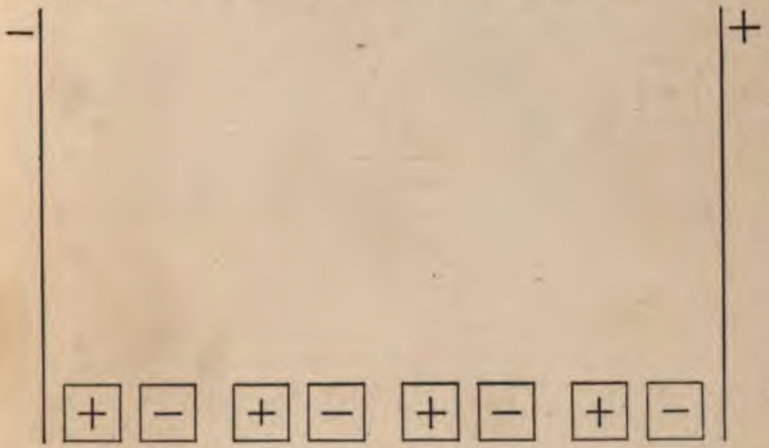

Fig. 36.

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[1] *Ann. de Chim.* [1], **58**, 54 (1806).

The atoms marked positive represent hydrogen; those marked negative, oxygen. Before the current is passed, each oxygen atom is combined with a certain definite hydrogen atom, forming water. When the current is passed, the hydrogen atom nearest the negative pole gives up its positive charge to that pole, — becomes electrically neutral, and separates as hydrogen gas. (See Fig. 37.) The oxygen atom which was originally in combination with this hydrogen is now free, and combines with the hydrogen of the next molecule of water. This sets another oxygen atom free, which combines with the next hydrogen, and so on until the positive pole is reached, when the last oxygen atom in the chain not having any hydrogen with which to combine, takes up positive electricity from the positive pole, becomes electrically neutral, and escapes as gaseous oxygen. The gases which escape only on the electrodes come from different molecules of water, as was made very probable by the experiment of Davy. The molecules between the electrodes are, during the electrolysis, constantly interchanging their constituents.

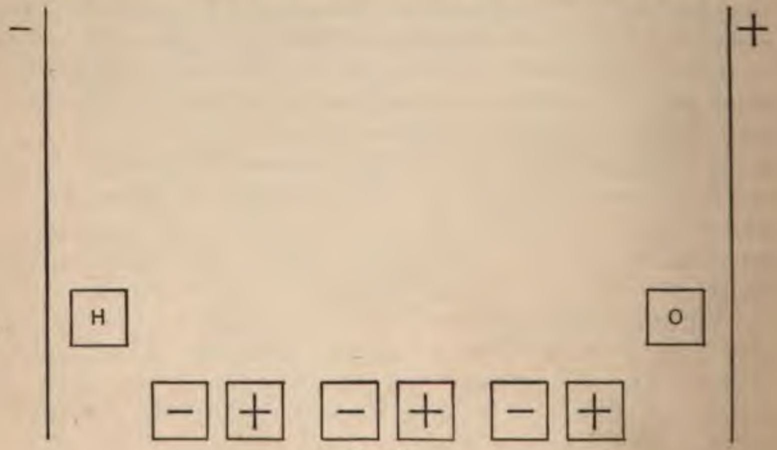
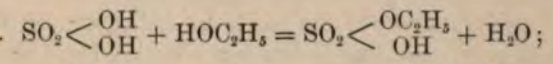


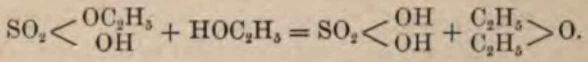
FIG. 37.

The distinctive feature of the theory of Grotthuss is that before electrolysis, each hydrogen atom is combined with a definite oxygen atom, from which it does not part company. The current must first decompose the water molecules before any electrolysis can take place. This theory accounted for the facts known at that time, and it remained as the established theory of electrolysis until after the middle of the nineteenth century.

Theory of Williamson. — A theory as to the condition of things in solution was proposed by Williamson[1] in 1851. This theory was the outcome of his work on the preparation of ordinary ether by the action of sulphuric acid on ethyl alcohol. The reaction which gave ether as the product was recognized as proceeding in the following stages: —

I. 

$$\mathrm{SO_2}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} + \mathrm{HOC_2H_5} = \mathrm{SO_2}<\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OH}\end{matrix} + \mathrm{H_2O};$$

II. 

$$\mathrm{SO_2}<\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OH}\end{matrix} + \mathrm{HOC_2H_5} = \mathrm{SO_2}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C_2H_5}\end{matrix}>\mathrm{O}.$$

The first stage of the reaction consists in the replacement of a hydrogen atom of the sulphuric acid by the ethyl group, with the elimination of a molecule of water.

The second consists in the replacement of the ethyl group in ethyl sulphuric acid, by the hydroxyl hydrogen atom from the alcohol. The reaction which takes place as represented in I is reversed in II, the final result being the removal of a molecule of water from two molecules of alcohol, and the formation of a molecule of ordinary ether. From this Williamson concluded "that in an aggregate of the molecules of every compound, a constant interchange between the elements contained in them is taking place."

Williamson[2] concluded his paper with the following very significant words: "In recent years chemists have added to the atomic theory an uncertain, and, as I believe, an unsubstantiated hypothesis, that the atoms are in a condition of rest. I reject this hypothesis and found my views on the broader basis, the *movement of the atoms.*"

Theory of Clausius. — Clausius[3] did not think it necessary or even justifiable to go as far as Williamson, and assume that there is a constant interchange of parts in a solution, and that no one part-molecule remains attached to another for any appreciable time. On the other hand, he saw that the theory of Grotthuss was not capable of accounting for facts which had come to light since it had been proposed. The current, according to Grotthuss, must first decompose the molecules before it can effect any electrolysis. In reference to this point Clausius[4] says: "In order to separate the once combined part-molecules, the attractions which they exert upon one another must be overcome. To accomplish this, a force of definite strength is necessary, and one is therefore led to the conclusion that as long as the force in the conductor does not possess this strength, no decomposition of the molecules can take place. But, on the contrary, when the force has acquired this strength, very many molecules must be decomposed at the same time, in that they are all under the effect of the same force, and have almost exactly the same position to one another. If the conductor conducts only by electrolysis, we may draw the following conclusion in reference to the current: As long as the driving force in the conductor is below a certain limit no current will pass, but when it has reached this limit a very strong current suddenly exists.

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[1] *Lieb. Ann.* **77**, 37 (1851).

[2] *Ibid.* **77**, 48 (1851).

[3] *Pogg. Ann.* **101**, 338 (1857).

[4] *Ibid.* **101**, 346 (1857).

"This conclusion is in direct opposition to the facts. The smallest force produces a current by alternate decomposition and reunion, and the intensity of the current increases according to Ohm's law, — proportional to the force. Therefore, the assumption that the part-molecules of an electrolyte are combined rigidly to form whole molecules, and that they have definite, regular, arrangement is erroneous."

The assumption, then, that the natural condition of a solution of an electrolyte is one of static equilibrium, in which every positive part-molecule is combined rigidly with a negative, was abandoned by Clausius as untenable and his own theory proposed in its place.

According to Clausius, an electrolytic solution consists mainly of whole molecules of the electrolyte, but in addition, there are some part-molecules. A positive part-molecule may, during the movements to which it is subjected, come into a position with respect to the negative part of another molecule, which is more favorable for union with this, than with its own negative companion. It would then part company with the latter and join the former. This would leave, then, a positive and a negative part-molecule free to move about through the solution and combine with other part-molecules, or break down whole molecules already existing as such in the solution. These movements and decompositions take place with the same irregularity as the heat movements which produce them. The two part-molecules resulting from the breaking down of a whole molecule, may combine directly with one another, or may be prevented from doing so by the movements due to heat. The amount of such decomposition in a solution would depend upon the nature of the solution and upon the temperature.

Allow an electric force to act upon a solution containing a mixture of whole and part-molecules. The part-molecules will no longer move about equally in all directions as they would if subjected to the action of heat alone, but more positive parts will move in the direction of the negative pole, and negative parts toward the positive pole, than in any other direction. This directing influence of the current will also facilitate the breaking down of the whole molecules into part-molecules.

This assumption of a partial breaking down of the molecules in a solution of an electrolyte, before any current is passed, accounted satisfactorily for the fact which could not be explained by the theory of Grotthuss — viz., that an infinitely weak current could effect electrolysis of water containing a little acid. Such a current, in terms of the theory of Clausius, would simply exert a directing influence on the part-molecules already present, since it would be too weak to break down any of the whole molecules of water. The amount of this directing influence would be proportional to the strength of the current, as had been shown to be the case. In the opinion of Clausius the action of the current is primarily a directing one, but, at the same time, it facilitates a decomposition of the molecules into part-molecules.

The theory of Clausius, which has just been considered at some length, will be recognized to be the father of the Theory of Electrolytic Dissociation. This brief historical sketch brings us up to modern electrochemistry.

ELECTRICAL ENERGY; UNITS; NOMENCLATURE

Electrical Energy. — Electrical energy may be factored into two factors, as already stated, — an intensity factor or potential, and a capacity factor or amount of electricity. This is analogous to the factors of heat energy; an intensity factor or temperature, and a capacity factor or amount of heat. The unit for the intensity factor of heat energy is the degree, starting from the absolute zero. We have no corresponding unit for the intensity factor of electrical energy, and may, therefore, choose our unit arbitrarily. We can start from any constant potential as zero. In practice, we usually select the potential of the earth as the zero point. The capacity for electrical energy is the amount present in a given system, for a definite difference in potential.

The relations between the different manifestations of energy, known as electricity and as heat, are striking and interesting; yet certain marked differences exist. One of these is so pronounced as to call for special comment.

Conduction of Heat and of Electricity. — All known substances conduct heat energy. Metals are the best conductors of heat, both as to quantity and rate. The best conductors of heat energy, however, as compared with the worst, hardly exceed the ratio of 100 to 1.

Substances behave very differently with respect to their power to transmit electrical energy. Those like the metals conduct electricity with the velocity of light, while glass, wax, etc., conduct with infinite slowness. The ratio between the best and poorest conductors of electricity is about as 10^{20} to 1.

Of the chemically pure substances, solids conduct in general better than liquids; yet, many non-conducting salts when fused become electrolytes. Gases, according to the recent work of J. J. Thomson,[1] undoubtedly conduct electrolytically.

Substances like the metals, which carry the current without undergoing chemical decomposition, are termed *conductors of the first class.*

Solutions of some substances in certain solvents are capable of conducting the current. Thus, acids, bases, and salts, in water, are conductors; but at the same time they undergo chemical decomposition. These are known as *conductors of the second class.* So little is known about the actual mode by which metals conduct the current, that it is difficult to say just how much importance should be attached to the distinction between metallic and electrolytic conduction. The most recent work, however, makes it very probable that there is a close relation between the two kinds of conductivity. It seems quite probable, though it has not been proved, that conductivity in metals, as well as in electrolytes, is ionic.

Law of Electrostatic Force (Coulomb's Law). — If two bodies are charged with electricity, the force acting between them depends upon the quantity of electricity upon the bodies, the distance between the bodies, and the nature of the medium which surrounds them. If we represent the quantities of electricity by q_1 and q_2, the distance between the bodies by d, and the specific inductive capacity or dielectric constant of the medium by C, the law of electrostatic attraction is expressed thus: —

$$F = \frac{1}{C}\frac{q_1 q_2}{d^2},$$

in which F is the force acting between the charged bodies.

This is known as the law of Coulomb, since it was he who first verified it experimentally.

Law of Joule. — Whenever conductors at different potentials are brought in contact, a current of electricity passes from one to the other. The current always flows from the conductor at higher to that at lower potential. During the passage of the current, certain effects are produced in the conductors which obey definite known laws. One of the most common of these is the heating of the conductor. Electrical energy disappears and heat energy appears. This fact must have been observed, qualitatively, by every one who has allowed a current to flow through a conductor. A quantitative relation between the resistance offered to the passage of the current, the strength of the current, and the amount of heat evolved was discovered experimentally by Joule.[1]

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[1] *Recent Researches in Electricity and Magnetism* (1893).

Let r be the resistance to the passage of the current, c the strength of the current, and h the amount of heat evolved in a given time; the following relation obtains:—

$$h = rc^2.$$

The heat evolved is proportional to the resistance and to the square of the strength of the current. This is the well-known law of Joule.

Law of Ohm.—A quantitative relation has also been established experimentally between the strength of the current, the electromotive force, and the resistance. Let C be the strength of the current, E the electromotive force, and R the resistance:—

$$C = \frac{E}{R},$$

which is Ohm's law.

Electrical Units.—There are two systems of units known respectively as the electromagnetic and electrostatic. The units in the two systems are very different. In the electromagnetic system, that current is taken as the unit, which, when passed around a circular conductor of radius 2π, will produce a magnetic intensity of 1 at the centre. When unit current flows one second, we have unit quantity of electricity.

In the electrostatic system, that quantity of electricity is taken as the unit, which, when placed at a distance of a centimetre from an equal quantity, the two being separated by air, will exert a force of a dyne, or will produce an acceleration in a gram weight of a centimetre per second. The nature of the medium separating the two quantities is essential to the definition, since the force exerted depends upon the dielectric constant of the medium.

The unit quantity in the electromagnetic system is very nearly 3×10^{10} times the unit quantity in the electrostatic system.

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[1] *Phil. Mag.* [3] **19**, 260 (1841).

The Electromagnetic System of Units. — The electromagnetic system has by far the widest application. In practice the unit of quantity is not that stated above, but one-tenth this amount.

The unit of potential is called a *volt.* The Clark element consisting of mercury, mercurous sulphate, zinc sulphate (saturated solution), amalgamated zinc, has an electromotive force of —

$$1.4328 - 0.0012\ (t^\circ - 15) \text{ volts.}$$

The unit of quantity most frequently used is called a *coulomb.* It is defined as the quantity which, when it falls one volt in potential, sets free 10^7 absolute units of energy. This, as stated above, is one-tenth of the electromagnetic unit.

The unit of energy is 10^7 in absolute units, and is called a *joule.*

When a coulomb passes in a second at a uniform rate, it gives a unit current, which is called an *ampère.*

The unit of resistance is that offered by a uniform column of mercury 106.3 cm. in length (containing 14.4521 grams) at 0°. It is called an *ohm.*

Electrostatic System. — The unit of quantity in the electrostatic system is, as stated above, much smaller than in the electromagnetic. The real electromagnetic unit of quantity is about 3×10^{10} as great as the electrostatic unit. But the electromagnetic unit actually in use — the coulomb — is only one-tenth of the true electromagnetic unit. Therefore, one coulomb $= 3 \times 10^9$ electrostatic units. The electrostatic unit is employed in measuring charges at rest. The unit of energy is the erg instead of 10^7 ergs, and the unit of potential is 300 volts.

Electrochemical Nomenclature. — We owe to Faraday the nomenclature in vogue even at the present day. The conduction of the current in a solution of an electrolyte is accompanied by a mechanical movement of the parts of the dissolved substance. These parts Faraday called *ions* or wanderers. Those moving in the direction of the positive current he called *cations*, and those in the opposite direction *anions.* The substances which conduct the current by undergoing decomposition he termed *electrolytes*, the decomposition effected by the current *electrolysis.* That portion of the conductors of the first class from which the current passes into the solution of the electrolyte he termed *electrodes.* That electrode toward which the cation moves he called the *cathode*, that toward which the anion moves the *anode.*

THE LAW OF FARADAY

Relation between Quantity of Electricity and Amount of Decomposition. — The law of Faraday, to which reference has already been made, is so important in connection with all electrochemical work that it should be considered more in detail. Faraday undertook a careful quantitative study of electrolysis, and determined the relation between the amount of electricity which passed through a solution of an electrolyte, and the amount of decomposition which it effects. He took into account the effect of changing the size and chemical nature of the electrodes, also the amount of electrolyte used. Further, he varied the amount of current which passed in a given time. In all cases he found that the amount of decomposition was the same for the same amount of current. He concluded that *the amount of decomposition effected by the current in a conductor of the second class is proportional to the amount of electricity which is passed through it.*

He then electrolyzed solutions of salts of several different metals by passing the same current through them in series, and weighed the metal which was deposited from each solution. He found that *the masses which separated were proportional to the combining weights of the elements.*

Where the ion is elementary, as in the case of a metal, the combining weight is equal to the atomic weight divided by the valency. Where the ion is complex, as is true especially of many anions, the combining weight is equal to the molecular weight of the ion divided by its valency.

These two facts lead to the following wide-reaching generalization: *The amounts of decomposition effected in all conductors of the second class by the passage of equal quantities of current are, for the same electrolyte, equal; for different electrolytes are proportional to the combining weights of the ions.*

From this, we see that chemically equivalent quantities of all ions have the same capacity for electrical energy. This is analogous to the law of Dulong and Petit, which says that all atoms have the same capacity for heat energy.

Testing the Law of Faraday. — Faraday[1] concluded from his own experiments that very small currents can pass through solutions of electrolytes without effecting chemical decomposition. The work of Shaw[2] on copper solutions showed slight deviations from the law of Faraday as the intensity of the current varied. This is supposed to be due to the solvent action of the solution of the copper salt on the copper which had already been precipitated. A careful quantitative study of the law of Faraday was made by Buff,[1] using the silver voltameter. The strengths of current employed varied as much as from 1 to 200, yet the law was always found to hold within the error of the experiment.

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[1] *Exp. Researches* (1834).

[2] *Brit. Ass. Report* (1886), 318.

Ostwald and Nernst[2] tested the law of Faraday for very small amounts of electricity, and showed that when 0.000005 coulomb is passed through a dilute solution of sulphuric acid, hydrogen is liberated at the cathode. They measured the amount of gas set free and the current which passed, and found that the law of Faraday held for such an infinitesimal quantity of electricity.

Some doubt was thrown a few years ago on the universal applicability of the law of Faraday. Solutions of electrolytes were electrolyzed under high pressure, and it was found that the amount of the electrolyte decomposed was less than would correspond to the law of Faraday. This has since been satisfactorily explained. Under the high pressure some gas dissolved in the water containing the electrolyte. This was slightly ionized in the solution, and helped to conduct the current. More current therefore passed than corresponded to the amount of the electrolyte decomposed.

Perhaps the most careful experimental test to which the law of Faraday has been subjected, and through which it has passed successfully, is in connection with the determination of the electrochemical equivalents of the ions.

The Electrochemical Equivalent. — If the quantities of all ions which stand to one another in the relations of their combining weights carry equal amounts of electricity, then it is of great scientific and practical importance to know the exact amount of electricity which a unit quantity of ions will carry. This can be determined by passing a given quantity of electricity through a solution of an electrolyte and weighing the amount of metal deposited upon the cathode, or measuring the amount of gas liberated. This has been done very carefully by Lord Rayleigh and Mrs. Sedgwick, who found that one coulomb of electricity deposits 1.11179 mg. of silver. W. and F. Kohlrausch, working with equal care, found under the same conditions 1.11183 mg. The mean of these values is 1.11181 mg. The mass of the ions taken as the unit is purely arbitrary. Here, as in so many other cases, it is convenient to use the gram-molecular weight for univalent, and gram-equivalent weight for polyvalent, ions. In case the ion is elementary and univalent, as with silver, the gram-molecular weight is identical with the gram-equivalent weight. The atomic weight of silver, in terms of oxygen $= 16$, is 107.93. In order to separate a gram-atomic weight of silver it will require $\frac{107.93}{0.0011181} = 96{,}530$ coulombs of electricity. This is the electrochemical equivalent.

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[1] *Lieb. Ann.* **85**, 1 (1853).

[2] *Ztschr. phys. Chem.* **3**, 120 (1889).

A more recent determination of the electrochemical equivalent of silver by Richards, Collins, and Heimrod[1] gives 0.0011172 g. of silver as equivalent to one coulomb.

A still more recent determination by Patterson and Guthe[2] gives the slightly larger value 0.0011192 g. of silver as equivalent to one coulomb. This agrees with the mean result obtained by Pellat and Portier, and is very close to the number obtained by Kahle (0.0011193).

The Voltameter. — The fact that a given amount of current always separates the same quantity of any metal from its salts, furnishes us with a simple and efficient method of measuring the amount of electricity which flows through any conductor in a given time. From the above figures it is clear that whenever a current deposits one milligram of silver from a solution of a silver salt, 0.8944 of a coulomb of electricity has passed through the solution. The principle of the voltameter is thus very simple. Suppose it is desired to know the amount of electricity which flows through a given conductor in a given time. The current is passed through a solution of some silver salt — say the nitrate — for the given length of time and the amount of silver deposited on the cathode determined. Knowing the amount of silver deposited, the calculation of the amount of electricity which has passed follows at once from what is given above.

This is not the place to discuss the details of the use of the silver voltameter. A general description of the apparatus should, however, be given. The form which, perhaps, is the most convenient consists of a platinum dish about three inches in diameter, which serves as the cathode. This is filled to a convenient depth with a 15 to 20 per cent solution of silver nitrate. A thick disk of silver serves as the anode. This is wrapped with a piece of fine linen, or filter paper, to prevent particles from dropping off from the anode into the dish. The current is connected directly with the anode. The platinum dish, serving as cathode, should rest in a wire frame which touches it at many points. After the experiment is over, the solution of silver nitrate is poured out of the dish, and the silver, which should be deposited uniformly and coherently upon the platinum, carefully washed and dried. The dish, which was weighed before the experiment began, is now reweighed. The gain in weight is the weight of the silver which has been deposited upon its surface.

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[1] *Ztschr. phys. Chem.* **32**, 321 (1900).

[2] *Phys. Rev.* **7**, 257 (1898).

Theoretically the salt of any metal which is deposited as such by the current might be used to measure the amount of the current. But practical difficulties come into play in many cases, so that only a few metals are well adapted to this purpose. Some of these difficulties may be indicated by stating that many metals do not separate uniformly upon the surface of the cathode and do not adhere firmly to it. In these cases it is difficult and often impossible to wash and weigh the deposit. Other metals easily undergo oxidation during deposition, or when exposed to the air in a finely divided state in washing and drying them. The metal best adapted to the uses of the voltameter is silver, and next to silver comes copper.

In addition to the metal voltameters, there is another form which depends for its utility upon the amount of gas set free when the current is passed through a dilute solution of sulphuric acid. In this form, which is called the *gas voltameter*, the gases are collected, reduced to standard conditions of temperature, pressure, and dryness, and then measured. A comparatively large volume of gas is liberated by a small amount of current. Thus, one gram of hydrogen ions carries 96,530 coulombs. One gram of hydrogen gas has a volume of 11,188 c.c. Since it is possible to measure a small part of a cubic centimetre of gas, it is possible to measure a very small quantity of electricity by means of the gas voltameter.

THE MIGRATION VELOCITIES OF IONS

Electrolysis. — The phenomenon of electrolysis shows that when a current is passed through a solution of an electrolyte, there is a mechanical movement of the ions of the electrolyte toward the electrodes. It becomes, then, a matter of interest and importance to determine the relative velocities with which the ions move, and also their absolute velocities under given conditions.

If we pass a current through a solution of copper sulphate, using copper electrodes, there will be a deposition of copper at the cathode, and exactly an equal amount of copper will pass into solution from the anode. The total amount of copper in solution will remain constant, but the color in the neighborhood of the anode will become deeper, while in the neighborhood of the cathode it gradually becomes less intense. The solution becomes more concentrated in copper around the anode and less concentrated around the cathode.

If in this experiment platinum electrodes are employed, copper would separate at the cathode; but since there is no metallic copper present to pass into solution, the amount in solution would become constantly less. In this case the color would disappear more rapidly around the cathode.

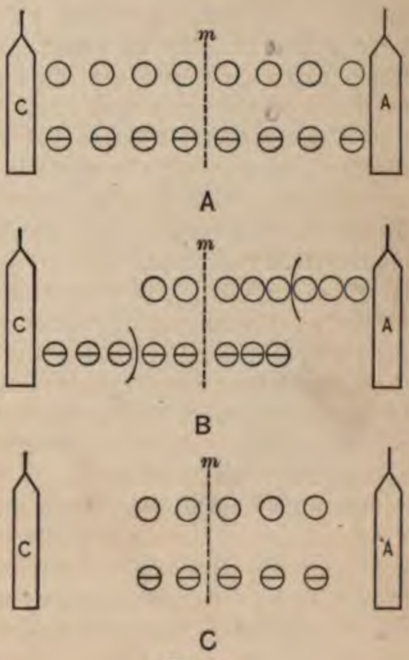

Fig. 38.

Hittorf's Theory.—Hittorf[1] explained these facts as due to the ions moving with different velocities through the solution—either the cation or the anion might have the greater velocity. That such an explanation can account for the facts, can be clearly seen from Fig. 38, which we owe in principle to Ostwald.[2] *A* represents the condition in the solution of the electrolyte before any current is passed. The white circles represent the anions, and the lined circles the cations. For each anion present in the solution there is a corresponding cation; and neither anions nor cations have separated at the electrodes. Let us take a case where the velocity of the anion differs greatly from that of the cation, and for the sake of simplicity let us say that the velocity of the anion is *twice* that of the cation. Let the current pass through the solution until three molecules have been electrolyzed, when the condition represented in *B* will exist. Three anions will have separated at the anode, and three cations at the cathode. But the solution of undecomposed electrolyte will have become relatively more concentrated on the anode side of the middle layer, marked *m*. Of the three molecules which have been decomposed and separated from the solution, two have come from the cathode side of the middle layer *m*, and one from the anode side, as is seen in *C*, which represents the solution after the electrolysis. If we divide the loss around the cathode by the total number of molecules electrolyzed, we shall obtain the value $\frac{2}{3}$. If, on the other hand, we divide the loss around the anode by the total number of molecules decomposed, the result is $\frac{1}{3}$. These two values bear the same relation to one another as the velocities of the anion and cation. From this we may draw two general conclusions: First, to find the relative velocity of the cation, divide the loss around the anode by the total amount of electrolyte decomposed. Second, to find the relative velocity of the anion, divide the loss around the cathode by the total amount of the electrolyte decomposed.

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[1] *Pogg. Ann.* **89**, 177; **98**, 1; **103**, 1; **106**, 337, 513 (1853–1859). Über die Wanderungen der Ionen. *Ostwald's Klassiker*, **21**, 22.

[2] *Lehrb. d. Allg. Chem.* II, 595.

There are, then, three quantities which can be determined experimentally: the change in concentration around the cathode, the change in concentration around the anode, and the total amount of the electrolyte decomposed. It is necessary to determine only two of these, since the third is given by the sum or difference. The two which are chosen depend upon the ease and accuracy involved in making the measurements.

Since the total amount of electrolyte decomposed is proportional to the amount of current which is passed through the solution, it is only necessary to measure the latter in order to know the former. This can be done conveniently by inserting a silver voltameter into the circuit, and weighing the amount of silver deposited. This is one of the quantities usually determined in carrying out such measurements.

Experimental Methods for Determining the Relative Velocities of Ions. — In determining the relative velocities of any given anion and cation, it is necessary to effect the electrolysis of a solution containing these ions, using as the electrodes the same metal as the cation. After the electrolysis has proceeded far enough to produce a determinable difference in concentration around the electrodes, and at the same time to leave a middle layer of unaltered concentration, the solution must be separated into two parts through the unaltered layer, and the change in concentration around one or both electrodes ascertained by analysis. The apparatus in which such determinations are carried out must be so constructed that the effect of diffusion, which would tend to mix the solutions of different concentrations around the electrodes, is reduced to a minimum.

Several forms of apparatus have been devised for determining the relative velocities of ions. Indeed, Hittorf,[1] in his own classical work upon this problem, devised a number of forms. In principle, however, they all closely resemble one another, and consist of a vertical tube divided into a number of compartments by means of horizontal diaphragms. Into the upper portion the cathode is inserted, into the lower the anode, around which the solution becomes more and more concentrated. After the electrolysis has been carried as far as desired, the solutions around the electrodes were removed and analyzed, and the changes in concentration thus determined. The membranes used in the forms of apparatus devised by Hittorf are objectionable, since they are liable to be acted upon by the electrolyte and produce indeterminable errors in the results. The more improved forms of apparatus for determining relative velocities avoid this source of error by doing away entirely with all membranes. The form devised and used by *Loeb and Nernst*[2] is essentially a Gay-Lussac burette. The electrode around which the solution will become more concentrated (usually the anode) is placed below. The electrolysis is carried on until there is considerable change in concentration around the electrodes, but it must be interrupted while there is still a middle layer of unaltered solution.

In carrying out a determination with this apparatus the corks and electrodes were placed in position and the whole weighed. The solution was then introduced through *C*, by closing *A* and evacuating *B* with the mouth. The apparatus is so constructed as to hold from 40 to 60 c.c. of solution. The openings at *C* and *B* are then closed, the whole apparatus placed in a thermostat and the current passed. After the electrolysis is ended, *C* is opened, and portions of the solution blown out, weighed, and analyzed. That part of the solution remaining in the apparatus

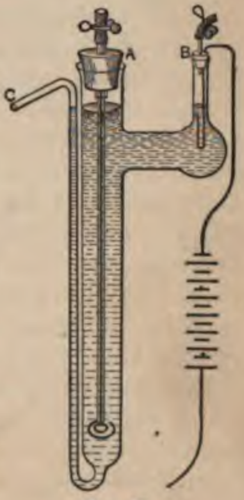

Fig. 39.

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[1] *Ostwald's Klassiker*, **21**, 22.

[2] *Ztschr. phys. Chem.* **2**, 948 (1888).

can be determined at any time by the gain in weight of the apparatus. The portion first removed contains the heavier, more concentrated solution around the anode; the second, the unaltered middle layer; and the third, the more dilute solution around the cathode.

This method is scarcely capable of any very high degree of accuracy. If it even overcomes satisfactorily the effect of diffusion, it is still open to a serious objection. After the electrolysis is ended there is no means by which the solutions of different concentrations can be completely separated from one another, removed, and analyzed. The method of blowing out the solution around the anode, together with enough of the unaltered middle layer to wash out the heavier solution, is not in keeping with the most refined work. From some work which has been carried out on this problem in this university, it seems better to measure the amount of current directly by means of a voltameter, than by any indirect method such as that employed by Loeb and Nernst.

The methods of *Kistiakowsky*[1] *and of Bein*[2] are the same in principle as that just described. The burettes are given different forms in the two cases, and also differ in form from the burette in the method just described. The same objection offered to the method of Loeb and Nernst applies here. There is no means of completely separating the two parts of the solution after the electrolysis is brought to an end. Quite recently Bein[3] has carried out an elaborate investigation on the velocities of ions, which, on the whole, probably contains some of the best results thus far secured. A large number of forms of apparatus are described, and much care and ingenuity are displayed in meeting special conditions. The means of separating the solutions, however, after the electrolysis is ended, could be improved.

A form of apparatus was recently devised in this university by *Mather*,[4] at the suggestion of the writer, which is free from some of the objections which can be urged against other forms. The form which was constructed and used successfully in a few cases is represented in Fig. 40. The following description of the apparatus is taken from Mather's dissertation: "The two limbs, *A* and *B*, are about 18 cm. in length and 2 cm. in diameter, and are then contracted above for an additional length of 6 cm. to a diameter of 0.5 cm.; the reduced portions being graduated in millimetres.

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[1] *Ztschr. phys. Chem.* **6**, 97 (1890).

[2] *Wied. Ann.* **46**, 29 (1892).

[3] *Ztschr. phys. Chem.* **27**, 1 (1898), **28**, 439 (1899).

[4] *Dissertation Johns Hopkins University* (1897). *Amer. Chem. Journ.* **26**, (1901).

These limbs are connected near the upper end of the large parts by a U-tube about 0.5 cm. in diameter, the bottom of which is some 2 cm. above the level of the lower ends of the limbs. At the centre of the tube is a stopcock, *S*, of large bore. The lower ends of the limbs are closed by glass stoppers (*G* and *H*), through which holes were bored for the insertion of the electrodes. In order to level the apparatus, and also to secure the same in the bath, the apparatus was cemented into a brass frame, which, by means of a clamp-screw, can be fastened to an upright rod upon the table or in the thermostat bath. The electric current, which was supplied by storage cells, was measured by means of two silver voltameters."

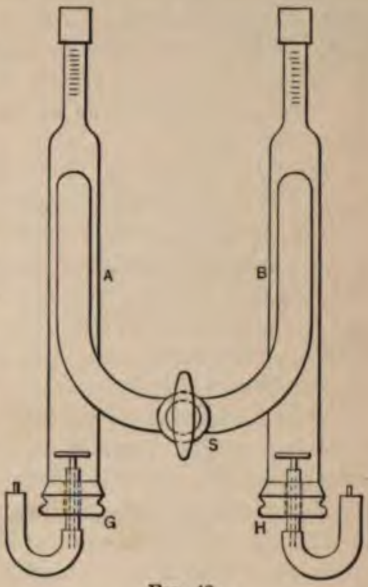

FIG. 40.

The apparatus was carefully calibrated before and after each experiment. The solution was introduced to a certain height in both arms, the apparatus being supported on a levelling stand. The apparatus and contents were placed in a constant temperature bath, and the current passed as long as desired. The stopcock was turned, and the solutions drawn out of both arms and analyzed — the changes in concentration being thus determined.

The great advantage of this apparatus over other forms is that after the electrolysis has been brought to an end the solutions on the two sides can be separated and washed out completely from the apparatus. In accurate work this is, of course, a matter of fundamental importance, and appears not to have been sufficiently regarded in much of the work which has already been done on the relative velocities of ions. Reference[1] only can be given to other recent investigations on the velocities of ions.

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[1] K. Hopfgartner: *Ztschr. phys. Chem.* **25**, 115 (1898). G. Kummel: *Wied. Ann.* **64**, 655 (1898). V. Gordon: *Ztschr. phys. Chem.* **23**, 469 (1897). O. Masson: *Ibid.* **29**, 501 (1899); *Phil. Trans.* **192**, A, 331. F. Kohlrausch: *Wied. Ann.* **66**, 785 (1899). A. A. Noyes: *Ztschr. phys. Chem.* **36**, 61 (1901). B. D. Steele, *Journ. Chem. Soc.* **79**, 414 (1901).

Causes which may affect the Relative Velocities of Ions. — It does not follow that the relative velocities of two ions obtained under one set of conditions is the same as the relative velocities under other conditions. This could be determined only by experiment. The effect of changing several of the conditions was studied by Hittorf.[1] He studied first the effect of *changing the strength of the current.* The currents in three determinations were of very different strengths.

The first precipitated 0.0042 g. silver in a minute.

The second precipitated 0.00113 g. silver in a minute.

The third precipitated 0.00958 g. silver in a minute.

The substance used was copper sulphate, and the relative velocities of copper and SO_4 were determined in the three cases, using the same concentration of the salt. The migration velocities of the copper in the three cases were 0.285, 0.291, and 0.289. From these results Hittorf concluded that the relative velocities are independent of the strength of current. This statement of Hittorf applies, of course, only to relative velocities. The absolute velocity with which the ions move is directly dependent upon the strength or driving power of the current.

The second question, says Hittorf,[2] which we must settle, has to do with the effect of *concentration* on migration velocity. Six solutions of copper sulphate of very different concentrations were subjected to electrolysis. Hittorf expresses the concentrations in terms of one part of copper sulphate to so many parts of water.

	PARTS WATER TO ONE PART COPPER SULPHATE	MIGRATION VELOCITY OF COPPER
1st solution	6.35	0.276
2nd solution	9.56	0.288
3rd solution	18.08	0.325
4th solution	39.67	0.355
5th solution	76.88	0.349
6th solution	148.30	0.362

The migration velocity of the copper with respect to the SO_4 increases as the dilution increases, until a certain dilution is reached. Beyond this it remains practically constant. It, however, does not follow from this that the velocity of the cation with respect to the anion always increases with increase in dilution. This is shown by the work of Hittorf[1] on solutions of silver nitrate.

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[1] *Pogg. Ann.* **89**, 177 (1853). *Ostwald's Klassiker*, **21**, 15.

[2] *Ostwald's Klassiker*, **21**, 17.

Parts Water to One Part Silver Nitrate	Migration Velocity of Silver
2.48	0.532
5.18	0.505
14.50	0.475
49.44	0.474
247.30	0.476

The velocity of the silver ion decreases as the dilution increases up to a certain limit, beyond which it remains constant.

It is possible that the explanation of such facts is to be found in the more complex ions which may exist in the more concentrated solutions. These may break down into simpler ions as the dilution increases. In measuring the relative velocities it is, therefore, necessary to work at dilutions so great that when the dilution is further increased the relative velocities remain unchanged.

There is a third condition according to Hittorf,[2] which may affect the migration, *i.e.* the effect of *temperature*. He concluded from his work on solutions of copper sulphate that between 4° and 21° the temperature coefficient was zero.

The work of Loeb and Nernst[3] on a few silver salts between 0° and 25° indicated that with rise in temperature all ions tend to move with the same velocity, which is 0.5. This point was investigated much more fully by Bein.[4] A few of his results for the anions will show that this conclusion is probably true.

	20°	75°	95°
Sodium chloride	0.608	——	0.551
Calcium chloride	0.602	——	0.549
Cadmium iodide	0.640	0.600	——
Silver nitrate	0.470 10°	——	0.490 90°

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[1] *Ostwald's Klassiker*, **21**, 22.

[2] *Pogg. Ann.* **89**, 177 (1853). *Ostwald's Klassiker*, **21**, 21.

[3] *Ztschr. phys. Chem.* **2**, 962 (1888).

[4] *Wied. Ann.* **46**, 29 (1892).

Migration Velocities a Periodic Function of Atomic Weights. — Bredig[1] pointed out that it had already been recognized that the migration velocities of elementary cations are a function, and a periodic function, of the atomic weights. Ostwald had already shown that this was true for elementary ions which consist of only one atom or element. Take the following anions and cations: —

	Velocity		Velocity		Velocity
Fl	50.8	Li	39.8	$\frac{1}{2}$ Mg	58
Cl	70.2	Na	49.2	$\frac{1}{2}$ Ca	62
Br	73.0	K	70.6	$\frac{1}{2}$ Sr	63
I	72.0	Rb	73.5	$\frac{1}{2}$ Ba	64
		Cs	73.6		
$\frac{1}{2}$ Cu	59	Ag	59.1	$\frac{1}{3}$ Al	42
$\frac{1}{2}$ Zn	54	Tl	69.5	$\frac{1}{3}$ Cr	61
$\frac{1}{2}$ Cd	55				

These relative velocities are plotted in a curve (Fig. 41). The ordinates represent velocities, and the abscissas atomic weights. A glance at the curve brings out the periodic nature of the velocities in terms of atomic weights. At, or very near the maxima of the curve we find the halogens. Here also we find the alkali metals. At the extreme minima we find aluminium and chromium.

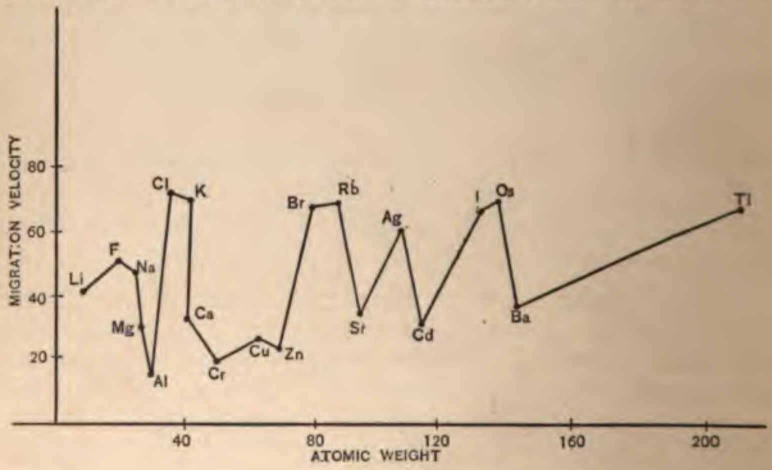

FIG. 41.

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[1] *Ztschr. phys. Chem.* 13, 242 (1894).

At breaks on the descending arms of the curve we find the members of the calcium group. Zinc and cadmium also occur near the minima. The significance of this periodic recurrence of velocities with respect to atomic weights is at present not known. Yet it is certainly an interesting fact, and another example of that periodicity among the properties of the elements which appears in so many directions.

The Absolute Velocities of Ions. — The methods hitherto considered give only the relative velocities with which the ions move. To determine the absolute velocities some other method must be employed. Two general methods have been employed for determining the absolute velocities with which ions move. The one is direct and measures at once the absolute velocities. This will be taken up here (Fig. 42).

There is also an indirect method of determining absolute velocities, involving the conductivity of solutions and the relative velocities. This will be taken up later under conductivity.

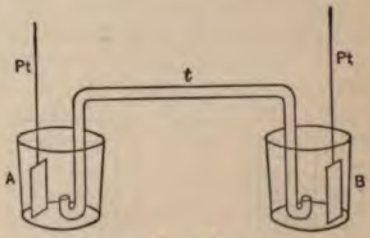

Fig. 42.

The Method of Lodge[1] for determining the absolute velocities of ions is the following: A glass tube *t*, 40 cm. long and 8 cm. wide, is graduated and bent at right angles near the ends. This is filled with an aqueous solution of gelatine, to which some sodium chloride had been added. The contents of the tube are colored red by phenolphthaleïn to which just a trace of alkali had been added to bring out the red color. One end of this tube passes into the larger vessel *A* (Fig. 42).

A piece of platinum foil is introduced into the vessel *A* and connected with a platinum wire so as to serve as an electrode. The other end of the tube *t* dips into a vessel *B*, into which an electrode is introduced as shown in the figure.

For the sake of simplicity and clearness let us suppose that both vessels *A* and *B* are filled with dilute sulphuric acid. A current is then passed from one electrode to the other through the tube *t*. The hydrogen ions move with the current from the vessel *A* into the tube *t*. They displace the sodium from the sodium chloride and from hydrochloric acid, which decolorizes the phenolphthaleïn.

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[1] *Brit. Ass. Report*, 1886, p. 393. Also 1887, 389.

After a given time the space in *t* over which the decolorization has extended is measured.

In making such measurements it is necessary to know the difference in potential at the two ends of the tube, or, as it is called, the drop in potential along the tube. A potential gradient of a volt a centimetre is taken as the unit. Knowing the drop in potential along the tube, the time during which the experiment has lasted, and the length of the tube in which the solution is decolorized, we have all the data necessary for calculating the absolute velocity of ions. For unit gradient, *i.e.* a drop in potential of one volt a centimetre, Lodge found the following velocity for hydrogen, which is the swiftest of all ions. 0.0026 cm. per second is the mean of three values which were found. These are 0.0029, 0.0026, and 0.0024 cm. per second. It will thus be seen that the absolute velocities of ions is very small indeed when subjected to a unit drop in potential.

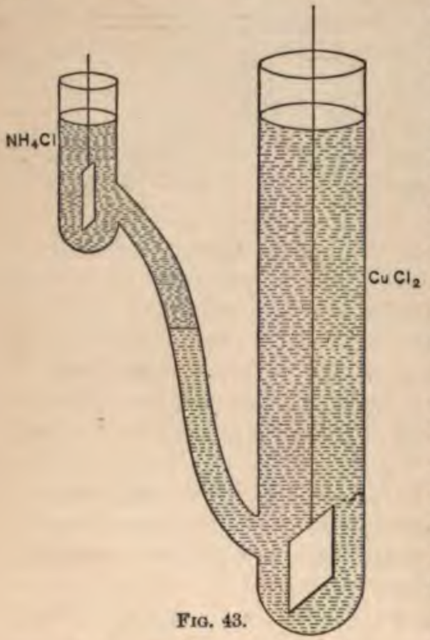

FIG. 43.

The results obtained by the indirect method already referred to will be compared a little later with those given by this direct method. The absolute velocities of a number of other ions, obtained by the indirect method, will also be given in the proper place.

The Method of Whetham[1] for measuring the absolute velocities of ions differs somewhat from that of Lodge. The apparatus used is seen in Fig. 43. Into each arm an electrode is inserted as seen in the figure.

Let us take two chlorides, the one colored and the other colorless, say copper and ammonium chlorides. The denser solution is introduced into the longer arm, and then the lighter solution is carefully poured into the shorter arm.

The current is now passed through the two solutions from the ammonium to the copper chloride. The cupric chloride is colored, due to the presence of copper ions. These, like the ammonium ions, move with the current; and consequently the bounding layer between the colorless and colored compound will move with the current. By noting the time of the experiment, the distance travelled by the bounding layer, and the potential gradient, Whetham could calculate the velocity of the copper ion.

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[1] *Phil. Trans.* 1893, A. 337.

The velocities of the copper ion and of the ion Cr_2O_7, obtained by Whetham, agree with those found by the indirect method to be considered hereafter.

THE CONDUCTIVITY OF SOLUTIONS OF ELECTROLYTES

Conductivity. — The conductivity of a substance is its power to carry the current. The conductivity of a conductor is the reciprocal of its resistance. The following relation between the resistance r, the current c, and the electromotive force π is expressed in Ohm's law: —

$$r = \frac{\pi}{c}.$$

The electromotive force π is the difference in the potential of the two ends of the conductor carrying the current. The reciprocal of the resistance, or the conductivity C, is, therefore, —

$$C = \frac{c}{\pi}.$$

Two units of resistance have been employed. The one most commonly used is that of a column of mercury 106.3 cm. in length and 1 sq. mm. in cross-section. The Siemens unit is that offered by a column of mercury 100 cm. long and 1 sq. mm. in cross-section.

Specific Conductivity. — The resistance offered by conductors depends upon two things, their nature and their form. To compare the resistances of different substances we must use forms which are comparable. There are two forms which have been used: that of a cube whose edge is 1 cm. long, and that of a cylinder 1 m. in length and 1 sq. mm. in cross-section. It is obvious that the resistance of the latter form is ten thousand times the former. When the resistance of such forms of substances is measured in ohms, it is known as the *specific resistance.* The *specific conductivity* is the reciprocal of the specific resistance.

These terms can be also applied to conductors of the second class. Such conductors are mainly solutions of some electrolyte in some dissociating solvent, and we must deal with comparable quantities of dissolved substances. In this case, as in so many others, we use gram-molecular weights of the different electrolytes.

Molecular Conductivity. — Place a litre of a normal solution of an electrolyte between two electrodes which are 1 cm. apart. Since the section of this solution is 1000 sq. cm., the conductivity of this solution will be 1000 times that of a cube of the same solution whose edge is equal to the distance between the plates. Let n be the number of cubic centimetres of a solution containing a gram-molecular weight of the electrolyte, and s the specific conductivity of the cube of the solution, then the molecular conductivity, which we will represent by μ, is expressed thus: —

$$\mu = ns.$$

If, on the other hand, we represent the specific conductivity of a cylinder of the solution 1 sq. mm. in cross-section and 1 m. in length by s, this will have $\frac{1}{10000}$ of the conductivity of the cube above described. The molecular conductivity μ would then be calculated thus: —

$$\mu = 10{,}000\, ns.$$

Since in the case of a normal solution $n = 1000$,

$$\begin{aligned}\mu &= s \times 10{,}000 \times 1000\\ &= s \times 10^7.\end{aligned}$$

The molecular conductivity, then, is equal to the specific conductivity referred to the cylinder unit, multiplied by 10^7.

Method of Measuring the Conductivity of Solutions. — A number of methods have been devised for measuring the conducting power of solutions. The earlier methods attempted to measure conductivity by means of a continuous current. But when such a current is passed through a solution, the electrodes become quickly polarized. This would increase the resistance of the solution, and seriously affect the result obtained. A number of attempts have been made to do away with the effect of polarization. Thus, Guthrie and Boyes abandoned the electrodes entirely, making use of induction currents in the solution. Others have used as the electrodes the same metal as the cation of the electrolyte. The chemical nature of the electrode would, then, not be changed when the current is passed. All of these methods have, however, given place to one which was devised by F. Kohlrausch,[1] in which an alternating current is used.

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[1] *Wied. Ann.* **6**, 145 (1879); **11**, 653 (1880); **26**, 161 (1885). *Pogg. Ann.* **138**, 280 (1869); **151**, 378 (1874); **154**, 1 (1875); **159**, 233 (1876).

The use of the alternating current makes us practically independent of the effect of polarization. A galvanometer cannot be used with an alternating current. A dynamometer may be used, but is less convenient and far more expensive than the ordinary telephone receiver, which answers every purpose.

In the Kohlrausch method, then, an alternating current is passed between platinum electrodes, through the solution whose conductivity it is desired to study. The resistance of the solution is balanced against a rheostat on a Wheatstone bridge, the point of equilibrium being determined by means of a telephone.

The apparatus used in the method of Kohlrausch is sketched in Fig. 44. *W* is a rheostat or set of resistance coils. The metre stick *AB* is divided into millimetres, and over this is stretched a manganine wire (manganine being an alloy of German silver and manganese). *J* is a small induction coil which furnishes the alternating current. *R* is a glass cup which contains the solution whose resistance is to be measured. The electrodes are cut from thick sheet platinum, and a piece of platinum wire is welded into the centre of each plate. This wire is then sealed into a glass tube, which is filled with mercury to make electrical contact with a copper wire introduced into the mercury. The telephone is connected between the rheostat and resistance vessel, and also with the bridge wire by means of a slider. The point of equilibrium is ascertained by moving the slider along the wire until the sound of the coil is no longer audible in the telephone. Let this be a point *C*. Let us call the distance *AC*, *a*, *BC*, *b*, the resistance in the box *r*, and the resistance

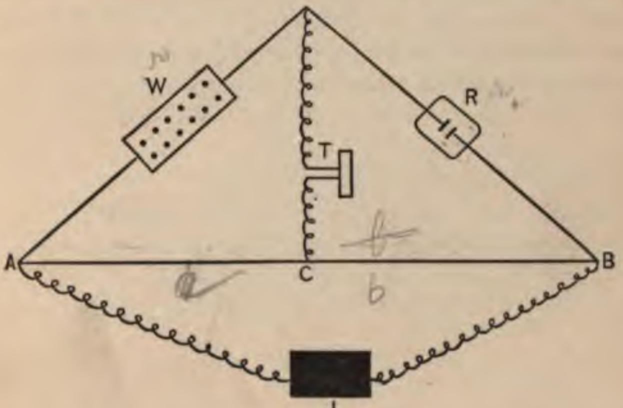

FIG. 44.

in the vessel r_1. From the principle of the Wheatstone bridge we would have —

$$rb = r_1 a;$$

$$r_1 = \frac{rb}{a}.$$

Since conductivity c is the reciprocal of the resistance r_1 —

$$c = \frac{a}{rb}.$$

This expression does not take into account the concentration of the solution. In practice it is best to express concentrations in terms of gram-molecular weights of the electrolytes in a litre (gram-molecular normal). As we have seen, the number of litres of the solution containing a gram-molecular weight of the electrolyte may be represented by n, when the above expression becomes —

$$c = \frac{na}{rb}.$$

By introducing n into the above expression, we pass from specific to molecular conductivities, and we express the molecular conductivity by the letter μ. In order to indicate the concentration n to which μ applies, we write for the molecular conductivity μ_n, —

$$\mu_n = \frac{na}{rb}.$$

This expression takes into account all of the factors except the cell constant k, which depends upon the size of the electrodes which we are using, and their distance apart. Introducing the constant, we have —

$$\mu_n = k\frac{na}{rb}.$$

Making a Conductivity Measurement. — If we examine the above equation, we shall find that there are two unknown quantities, μ_n and k. The first step in applying the Kohlrausch method is, then, to determine the value of one of these unknown quantities, and, in fact, the value of the cell constant k. In order to determine k, some solution must be used whose value of μ_n is known. The concentration n must be known, and a, b, and r, ascertained. The solution most commonly employed is a $\frac{\textit{normal}}{50}$ solution of potassium chloride. At 25° the conductivity of this solution, or the value of μ_n, $= 129.7$.

This solution is poured into the cell until both electrodes are covered. The cell is then placed in the thermostat, and the solution warmed to 25°. The readings are then made on the bridge, and the value of k calculated. The value of k having been determined, the cell is ready for conductivity measurements.

Before the constant of the cell is determined, it is necessary to cover the electrodes with platinum black in order to secure a sharper minimum in the telephone. This is effected by electrolyzing in the cell a dilute solution of platinic chloride. The current is passed first in one and then in the other direction, until both plates are covered with the finely divided platinum.

In order to measure the conductivity of any substance a solution of known concentration must be prepared. This is poured into the cell until the electrodes are covered. The cell is then placed in the thermostat and its contents brought to the desired temperature. The coil is started and the readings a and b determined, n having been noted.

All of the quantities in the conductivity equation are thus known except μ_n, which is calculated at once.[1]

Conditions which must be fulfilled in Making Conductivity Measurements. — In order that accurate conductivity measurements may be made by the method of Kohlrausch, it is desirable that the wire on the bridge should have uniform resistance throughout. If this is not the case, as in fact it never is, *the wire must be calibrated* and corresponding corrections applied. The most convenient method of calibrating a wire is that devised by Strouhal and Barus.[2] The principle of the method is analogous to that which is employed in calibrating a thermometer, when a thread of mercury is broken off from the column and moved along the capillary, the space occupied in each position being noted. For a detailed description of the method some laboratory guide[3] must be consulted.

Another factor of prime importance in all conductivity measurements is the *conductivity of the water* which is used as the solvent. When we measure the conductivity of a solution of an electrolyte in water, we actually measure the sum of the conductivities of the water and of the electrolyte. In order to know the conductivity of the electrolyte, it is necessary to know that of the water used, in order that it may be subtracted from the conductivity as measured.

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[1] For details in connection with the Conductivity Method, see *Freezing-point, Boiling-point, and Conductivity Methods*, by Jones (Chem. Pub. Co., Easton, Pa.).

[2] *Wied. Ann.* **10**, 326 (1880).

[3] Traube: *Physikalisch-chemische Methoden.* Jones: *Freezing-point, Boiling-point and Conductivity Methods.* Ostwald: *Hand- und Hilfsbuch zur Ausführung Physiko-chemische Messungen.*

For conductivity work it is very desirable to have water of a high degree of purity. A large number of methods have been suggested for purifying water for such purposes. The purest water which has ever been obtained was prepared by Kohlrausch and Heydweiller.[1] Water of a high degree of purity was distilled in a vacuum, and its conductivity determined without allowing it to come in contact with the air. The degree of purity attained by this method is best realized by the following comparison of the conductivity of the water with that of a metal. A cubic millimetre of this water at zero degrees had a resistance which was equal to that of a copper wire one millimetre in diameter extending around the earth one thousand times.

It is not possible, nor is it at all necessary, to prepare water of this degree of purity for ordinary conductivity work. In such work comparatively large quantities of water are needed, and methods are available for obtaining an abundance of water of a high degree of purity.

A method has been devised by Jones and Mackay[2] in which the water is twice distilled, but the process is a continuous one. Ordinary distilled water is placed in a large balloon flask, and some potassium bichromate (or potassium permanganate) and sulphuric acid added. When this water is boiled, the organic matter is burned up, and the ammonia held back as the sulphate. The vapor from this flask is led into a large retort containing an alkaline solution of potassium permanganate, which absorbs the carbon dioxide. The water vapor is then condensed in a tube of block tin, and received in a glass bottle which has been cleaned with especial care. By this method from five to six litres of water can be obtained daily, having a conductivity of from 1.5 to 2×10^{-6}. This is sufficiently pure for general conductivity work. The correction which must be applied to the values of μ_n for the conductivity of water of this degree of purity, is so small that it can be entirely neglected in the more concentrated solutions. It attains an appreciable value only in the more dilute solutions. Other methods of purifying water have been described by Nernst[3] and Hulitt.[4]

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[1] *Ztschr. phys. Chem.* **14**, 317 (1894).

[2] *Ibid.* **22**, 237 (1897). *Amer. Chem. Journ.* **19**, 91 (1897).

[3] *Ztschr. phys. Chem.* **8**, 120 (1890).

[4] *Ibid.* **21**, 297 (1896).

Temperature Coefficient of Conductivity. — There are few properties affected by temperature to the same extent as the conductivity of solutions.

Great care must therefore be taken to keep the temperature constant during conductivity measurements. For this purpose any accurate thermostat may be used. It is necessary in all such work that a thermoregulator be employed, which shall keep the temperature constant to within a tenth of a degree.

A thermostat well adapted for conductivity measurements is that devised and used by Ostwald,[1] and this is now generally employed wherever conductivity work is done. The thermostat bath contains a large volume of water to reduce the effect of changes in the temperature of the surrounding objects. A large glass tube containing a ten per cent solution of calcium chloride is placed in the bath, and connects above with an Ostwald regulator. The temperature of the bath is regulated by the expansion and contraction of the solution of calcium chloride, which has a large temperature coefficient of expansion. The Ostwald thermoregulator is shown in Fig. 45. The bottom of the U-shaped tube is filled with mercury, as shown in the figure. Gas enters at *A*. The tube *A* is inserted into one arm of the regulator, and shoved down until it nearly touches the mercury. This tube also contains a small hole in the side. When the bath becomes warmer than the regulated temperature, the solution of calcium chloride expands, drives up the right arm of mercury, and cuts off the gas. The small hole in the side of *A* prevents the flame from becoming extinguished. When the bath cools the solution contracts, the mercury falls in the right arm, and opens the end of the tube *A*, when an abundance of gas escapes and the size of the flame beneath the thermostat bath increases. Thus the regulator works automatically.

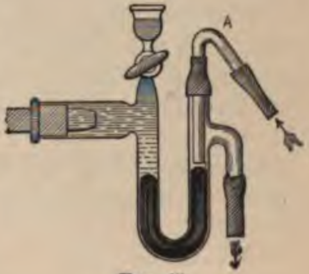

FIG. 45.

The solution whose conductivity it is desired to measure is placed in the resistance vessel, and the vessel suspended in the thermostat bath. The solution is stirred by raising and lowering the electrodes, and should be allowed to remain in the bath at least an hour at constant temperature, in order to insure that temperature equilibrium has been established.

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[1] *Ztschr. phys. Chem.* **2**, 565 (1888).

The Relative Conductivities of Different Substances. — The first generalization reached through the study of the conductivities of aqueous solutions of different substances, is that chemical compounds can be divided into two large classes. First, those which in the presence of water conduct the current, undergoing simultaneously decomposition or electrolysis. These are called *electrolytes.* Second, those substances which, in the presence of water, do not conduct the current, and do not undergo any decomposition when an attempt is made to pass a current through their solutions. These are called *non-electrolytes.*

The electrolytes themselves differ greatly in their conducting power. They may be divided roughly into two classes: Those with high conductivity, as the strong acids, strong bases, and salts; and those with low conductivity, as the organic acids and bases. This division into two classes is more or less arbitrary, since among the electrolytes we find nearly every degree of conductivity represented. It is true, however, that most substances which conduct belong near the extremes. Again, we recognize marked differences between the good conductors. The strong monobasic acids, such as hydrochloric, hydrobromic, nitric, etc., are the best conductors. The strong bases, such as sodium and potassium hydroxides come next in order, and then the salts.

Demonstration of the Different Conductivities of Different Substances. — It can be readily demonstrated that different electrolytes have very different conductivities. This has been shown by Noyes and Blanchard[1] in an experiment which they state was devised by Whitney. Prepare half-normal solutions of hydrochloric, sulphuric, chloracetic, and acetic acids. Introduce these into four glass tubes, *A*, *B*, *C*, *D*, about 20 cm. long and 3 cm. internal diameter, as shown in Fig. 46. These glass tubes are closed by rubber stoppers, through which pass glass tubes. These tubes carry copper wires, the wires

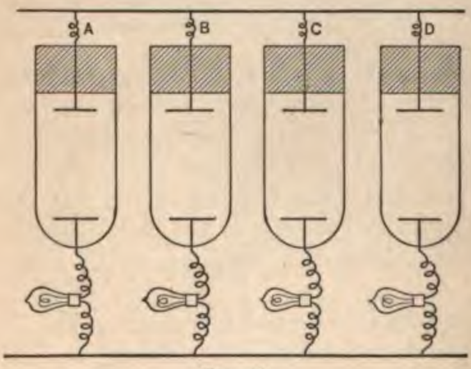

FIG. 46.

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[1] *Journ. Amer. Chem. Soc.* **22**, 736 (1900).

terminating in platinum disks as shown in the figure. We must be able to move these glass tubes through the rubber stoppers. The wire coming from the bottom of each tube is connected with a 32 candle-power, 110-volt lamp. The other side of each lamp is connected with one wire from a 110-volt, alternating-current dynamo. The wires from the tops of the glass tubes are connected with the other wire from the dynamo.

Add 100 cc. of pure water to each glass tube. Add 5 cc. of the solution of hydrochloric acid to the tube *A*; add an equal quantity of the sulphuric acid to the tube *B*; of chloracetic acid to the tube *C*; and of acetic acid to the tube *D*. After each solution has become homogeneous, close the circuit in a dark room, and so adjust the height of the upper electrode that all the lamps are equally brilliant. Then examine the heights of the electrodes in the four cylinders. If in the hydrochloric acid the upper electrode is at the top of the cylinder, in the sulphuric acid it will be about one-fourth from the top, in the chloracetic acid about three-fourths from the top, and in the acetic acid the electrodes will nearly touch.

This shows the different amounts of dissociation of the four acids at the same concentration — the hydrochloric acid being the most, the acetic acid the least, dissociated.

This experiment can be used to illustrate another fact. If the acid in each cylinder is just neutralized with sodium hydroxide, and the experiment repeated as above, the electrodes being adjusted so that all the lights are equally brilliant, it will be seen that the distance between the electrodes in the four cylinders is very nearly the same, showing that the sodium salts of all four acids are equally dissociated.

Increase in Molecular Conductivity with Increase in Dilution. — The study of the relation between molecular conductivity and dilution of the solution soon led to the conclusion that the molecular conductivity increases with the dilution. The resistance of a solution increases with the dilution, which is the same as to say that the actual conducting power decreases as the dilution increases. While this is true, the conductivity does not decrease as rapidly as the dilution increases, hence the molecular conductivity increases with the dilution. There are so few exceptions known to this generalization that it may be regarded as almost a general truth.

This increase in molecular conductivity with increase in dilution is, however, not unlimited. The molecular conductivity of the best conductors becomes constant at a dilution of from 1000 l. to 10,000 l., and remains constant from this point, however far the dilution may be carried.

The same general relations hold for the poorer conductors, but in these cases the constant value of the molecular conductivity is reached only at dilutions much greater than those named above. For many of the poorest conductors, the constant value of the molecular conductivity cannot be obtained directly by the conductivity method. In such cases an indirect method must be applied, as we shall see later.

The facts stated above in reference to the good conductors can be seen more clearly by examining a few data obtained with an acid, a base, and a salt, at different concentrations. v is the volume of the solution in litres which contains a gram-molecular weight of the electrolyte; μ_v is the molecular conductivity at the dilution v.

HYDROCHLORIC ACID		SODIUM HYDROXIDE		POTASSIUM CHLORIDE	
v	μ_v 18°	v	μ_v 18°	v	μ_v 18°
0.333	201.0	0.333	100.7	0.333	82.7
1.0	278.0	1.0	149.0	1.0	91.9
10.0	324.4	10.0	170.0	10.0	104.7
100.0	341.6	100.0	187.0	100.0	114.7
500.0	345.5	500.0	186.0	500.0	118.5
1000.0	345.5			1000.0	119.3
				10,000.0	120.9

The maximum constant value which μ_v attains at high dilution is termed μ_∞, and its significance will be seen when we study the application of the conductivity method to the measurement of electrolytic dissociation.

These results serve also to illustrate the three degrees of conductivity possessed by the good conductors, — acids, bases, and salts.

The Law of Kohlrausch. — A relation of wide-reaching significance was discovered by Kohlrausch by comparing the values of μ_∞ for different substances. He found that the difference between the values of μ_∞ for two electrolytes having a common anion and different cations, is the same as the difference between the values of μ_∞ for any two electrolytes having a common anion, and the same cations as the above electrolytes. An example will make this clear:

The value of μ_∞ for potassium bromide at 18° is . . .	141.0
The value of μ_∞ for sodium bromide at 18° is . . .	120.0
Difference	21.0

The value of μ_∞ for potassium nitrate at 18° is	121.0
The value of μ_∞ for sodium nitrate at 18° is	97.5
Difference	23.5

The same relation obtains for a common cation as for a common anion. In this case the difference between the values of μ_∞ for two electrolytes having a common cation and different anions is the same as the difference between the values of μ_∞ for any two electrolytes having a common cation and the same anion as the electrolytes in question. This can be seen from the example given: —

$$\mu_\infty \text{KBr} - \mu_\infty \text{KNO}_3 = 141 - 121 = 20.0;$$
$$\mu_\infty \text{NaBr} - \mu_\infty \text{NaNO}_3 = 120 - 97.5 = 22.5.$$

The difference between the two values is hardly larger than the experimental error.

The value of μ_∞ for any electrolytes is, then, the sum of two constants, the one depending on the anion and the other on the cation. The conductivity of a solution depends on the number of ions present, and the velocity with which they move. The value of the molecular conductivity at complete dissociation, since it deals with comparable quantities of ions, depends on the velocities with which the ions move. The value of μ_∞ for any substance depends on the velocities of the ions into which the substance dissociates. The constants above referred to, are, then, proportional to the velocities of the cation and anion respectively. If we represent by c the velocity of the cation, and by a the velocity of the anion, —

$$\mu_\infty = c + a.$$

Expressed in words, *the velocity with which any ion travels is a constant for a given solvent and a given potential gradient, and is independent of the nature of the other ion or ions with which it is present in the solution.*

This generalization is usually referred to as the law of the independent migration velocities of ions. The law in this form holds, in general, only for very dilute solutions, since it is only in such solutions that the true values of μ_∞ are obtainable directly by experiment.

Ostwald's Modification of Kohlrausch's Law. — The law as enunciated by Kohlrausch applies only to very dilute solutions. Ostwald[1] has shown that the law of Kohlrausch is of general applicability, and can be used with more concentrated as well as with more dilute solutions. If, however, the solutions are more concentrated and not completely dissociated, the amount of their dissociation must be taken into account. If we represent this, as is usually done, by α, the law of Kohlrausch as applied to incompletely dissociated solutions becomes —

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[1] *Lehrb. d. Allg. Chem.* II, 672.

$$\mu_v = \alpha (c + a).$$

As the dilution increases α approaches more and more nearly to unity, and when the dissociation is complete it becomes unity. The Ostwald modification of the Kohlrausch law becomes, at this point, identical with the original law proposed by Kohlrausch.

The Law of Kohlrausch used to determine the Velocity of Ions. — It is obvious from what has already been said, that the law of Kohlrausch can be used to determine the velocity of ions. The law states that for completely dissociated solutions the velocity of the cation c, plus the velocity of the anion a, is a constant. The value of this constant, or μ_∞, is determined at once by applying the conductivity method to completely dissociated solutions, and measuring the molecular conductivity. In a word, we can determine at once the value of $c + a$. We determine the value of $\frac{c}{a}$ by the Hittorf method of determining relative migration numbers. Knowing $c + a$ and $\frac{c}{a}$, we obtain at once absolute values for the velocities of both ions.

If this method is correct, then the velocity of any given ion must be the same, whether determined from one substance, or from any other substance in which it may occur. This was tested by Kohlrausch[1] for the chlorine ion. The velocity of this ion was calculated from several salts and was found to be the same in each case. The velocities are expressed in 10^{-6} centimetres per second. The potential gradient is 1 volt per centimetre; the temperature, 18°.

Concentration Normal	KCl			NaCl			LiCl		
	$c+a$	c	a	$c+a$	c	a	$c+a$	c	a
0.1	1153	564	589	952	360	592	853	259	594
0.01	1263	619	644	1059	415	644	962	318	644
0.001	1313	643	670	1110	440	670	1013	343	670
0.0001	1335	654	681	1129	448	681	1037	356	681

The results for the velocity of the chlorine ion are the same for the different salts.

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[1] *Wied. Ann.* **50**, 385 (1893).

Kohlrausch[1] determined the velocities of a number of ions in centimetres per second, under unit potential gradient, *i.e.* a drop in potential of one volt a centimetre.

CATIONS	VELOCITY IN CENTIMETRES PER SECOND
Hydrogen	0.00320 cm.
Potassium	0.00066 cm.
Sodium	0.00045 cm.
Lithium	0.00036 cm.
Ammonium	0.00066 cm.
Silver	0.00057 cm.

ANIONS	VELOCITY IN CENTIMETRES PER SECOND
Hydroxyl	0.00182 cm.
Chlorine	0.00069 cm.
Iodine	0.00069 cm.
Nitro group	0.00064 cm.

It will be seen that hydrogen is the swiftest of all ions, and that hydroxyl comes next with respect to its velocity. It will, however, be observed that even the swiftest ions move very slowly through the solvent in which they are contained.

APPLICATIONS OF THE CONDUCTIVITIES OF SOLUTIONS OF ELECTROLYTES

The Dissociation of Electrolytes.—The most important application of the conductivity of electrolytes is to measure their dissociation. If the dissolved substance is not dissociated at all, the conductivity would be zero. If it were completely dissociated, the conductivity would be a maximum. If it were partly dissociated, the conductivity would lie somewhere between zero and the maximum value. Since conductivity and dissociation are proportional, to determine the latter it is only necessary to divide the conductivity at the dilution in question by the conductivity at complete dissociation. The conductivity at any dilution, v, is represented by μ_v. The conductivity at complete dissociation is represented by μ_∞; the percentage of dissociation, by α. We have the following relation:—

$$\alpha = \frac{\mu_v}{\mu_\infty}.$$

It is very simple to determine the value of μ_v for any dilution of any electrolyte in water. It is only necessary to apply the Kohlrausch method directly, and calculate the molecular conductivity.

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[1] *Wied. Ann.* **50**, 403 (1893).

It is not always such a simple matter to determine the value of μ_∞. Some of the more complicated cases will be considered.

Determination of the Maximum Molecular Conductivity. — If the compound is strongly dissociated, such as the strong acids and bases, and the salts, the value of μ_∞ is determined by increasing the dilution of the solution until a value for the molecular conductivity is reached which remains constant.

If, on the other hand, the compound is not strongly dissociated, it is not possible to determine μ_∞ by the above procedure. The dilution at which the dissociation would be complete is so high that it is not possible to use the conductivity method with any degree of accuracy. An indirect method of determining μ_∞ for the weakly dissociated substances has been worked out and applied. Let us take first the weak acids, say the organic acids. These acids dissociate like all other acids into a hydrogen cation and a complex organic anion. If the hydrogen of the acid is replaced by a metal, we have a salt formed, and all salts are strongly dissociated substances. The value of μ_∞ for the salt can be determined readily by means of the conductivity method. Ostwald used the sodium salt. The value of μ_∞ for this compound is from Kohlrausch's law the sum of two constants, the one depending upon the anion and the other on the cation. If from the value of μ_∞ for the sodium salt we subtract the constant for the sodium ion, which is known, the remainder is the constant for the anion. If to this constant we add the constant for hydrogen, we have the value of μ_∞ for the acid, since all acids are made up of an anion and the cation hydrogen. The value of the constant for the sodium ion at 25°, as given by Ostwald, is 49.2, and that of the hydrogen ion 325. The value of μ_∞ for an acid at 25° is the value of μ_∞ for the sodium salt of that acid, minus 49.2, plus 325; *i.e.* μ_∞ for the sodium salt plus 275.8.

If we wish to determine μ_∞ for a weak base, we proceed in a strictly analogous manner. The nitrate or chloride of the base is prepared. This being a salt is strongly dissociated, and the value of μ_∞ for the chloride or nitrate can be determined directly by the conductivity method. The value of μ_∞ for the chloride of a base is the sum of two constants, the one depending upon the cation of the base, and the other upon the chlorine anion. The value of μ_∞ for the free base is the value of μ_∞ for the chloride, minus the constant for chlorine, plus the constant for hydroxyl. The value of the constant for chlorine at 25° is 70.2; that of hydroxyl, 170. The value of μ_∞ for the base is, then, the value of μ_∞ for the chloride, minus 70.2, plus 170, or plus 99.8. If the nitrate is used the value of the constant for the NO_3 anion is 65.1. To obtain μ_∞ for the base we must, therefore, add 104.9 to the value of μ_∞ for the nitrate of the base.

An empirical method has been worked out by Ostwald[1] for determining the value of μ_∞ for the sodium salt of an acid, from the value of μ_v at any ordinary concentration. As the result of the study of a large number of acids he found that μ_v at a given volume differed by a constant quantity from μ_∞. These differences for volumes ranging from 32 to 1024 l. are given below:—

Volumes:	32	64	128	256	512	1024
Differences:	12	10	8	6	4	2

By adding these differences to μ_v at any of the above volumes, we obtain μ_∞ at once. Knowing the value of μ_∞ for any compound, and also the value of μ_v, we obtain at once the dissociation α — which is equal to μ_v divided by μ_∞.

Comparison of Dissociation from Conductivity with Dissociation from Freezing-point Lowering. — We have thus far studied two methods of measuring electrolytic dissociation, — the conductivity and freezing-point methods. The question is whether the results obtained by the two methods for the same substance at the same dilutions, are the same, or different. A few results will answer this question. In the following table the conductivity measurements were made by Kohlrausch, the freezing-point measurements by Jones[2]:—

Compounds	Concentration Gr. Molec. Normal	Dissociation from Conductivity	Dissociation from Freezing-point Lowering
		Per Cent	Per Cent
NaCl . . .	0.001	98.0	98.4
NaCl . . .	0.01	93.5	90.5
NaCl . . .	0.1	84.1	84.1
K_2SO_4 . .	0.001	92.3	94.2
K_2SO_4 . .	0.005	85.8	88.7
K_2SO_4 . .	0.05	70.1	72.6
$ZnCl_2$ . .	0.001	94.5	95.5
$ZnCl_2$ . .	0.005	88.3	89.8
$ZnCl_2$ . .	0.05	74.1	79.4
HCl . . .	0.002	100.0	98.4
HCl . . .	0.01	98.9	95.8
HCl . . .	0.1	93.9	88.6

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[1] *Lehrb. d. Allg. Chem.* II, 693.

[2] *Phil. Mag.* **36**, 465 (1893).

COMPOUNDS	CONCENTRATION GR. MOLEC. NORMAL	DISSOCIATION FROM CONDUCTIVITY	DISSOCIATION FROM FREEZING-POINT LOWERING
		Per Cent	Per Cent
H_2SO_4 . .	0.003	89.8	86.0
H_2SO_4 . .	0.005	85.4	83.8
H_2SO_4 . .	0.05	62.3	60.7
KOH . . .	0.002	100.0	98.4
KOH . . .	0.01	99.2	93.7
KOH . . .	0.1	92.8	83.1
NH_4OH . .	0.006	16.6	11.1
NH_4OH . .	0.01	13.0	6.9
NH_4OH . .	0.05	6.1	3.8
K_2CO_3 . .	0.003	92.0	96.6
K_2CO_3 . .	0.005	88.6	96.0
K_2CO_3 . .	0.05	71.9	77.5

The results obtained by the two methods agree, in general, about as well as could be expected, if we consider that the conductivity measurements are made at 18° and the freezing-point measurements at, and slightly below, 0°. In some cases differences larger than can be accounted for in this way are apparent, but these are probably due to experimental errors in one or both methods.

The Dilution Law of Ostwald. — Since the molecular conductivity of solutions of electrolytes increases with the dilution, and since dissociation is proportional to conductivity, it follows that dissociation increases with the dilution of the solution. This holds up to a certain point, as we have seen. Beyond a certain dilution the conductivity remains constant, which means that the dissociation at this dilution is constant. For the good conducting substances the molecular conductivity increases slowly with the dilution. It increases much more rapidly for the poorer conductors, such as the organic acids and bases. The difference between the molecular conductivities of the good and bad conductors thus become less as the dilution increases.

Ostwald[1] found from his own work that the molecular conductivities of all monobasic acids pass through the same series of values. Thus, if any two acids A and B have the same molecular conductivities at volumes v_1 and v_2, they will have the same conductivities at any other volumes. Ostwald[2] went much farther, and discovered the mathematical expression connecting dissociation and dilution. He gave us our first rational dilution law. The law was deduced as follows: —

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[1] *Journ. prakt. Chem.* **31**, 433 (1885).

[2] *Ztschr. phys. Chem.* **2**, 36, 276 (1888); **3**, 170 (1889).

If the laws of gas-pressure hold for dilute solutions, and if the Arrhenius theory of electrolytic dissociation to account for the exceptions shown by electrolytes is true, then the formula connecting the degree of dissociation with the volume of gases must apply directly to the relation between the dilution and the dissociation of electrolytes.[1] The law of the dissociation of gases must apply also to the dissociation of dilute solutions.

For a homogeneous system of one volume of a gas dissociating into two volumes of gaseous products, Ostwald[2] deduced the formula:

$$R \log \frac{p}{p_{\text{I}} p_{\text{II}}} = \frac{q}{T} + \text{const.}$$

p, p_{I}, and p_{II} are, respectively, the pressures of the undissociated gas and of the decomposition products. q is the heat of decomposition.

If the temperature is constant and neither of the decomposition products is present in excess, the above expression becomes —

$$\frac{p}{p_1^2} = \text{const.} \tag{1}$$

p is the pressure of the undissociated gas, and p_1 that of the decomposition products.

Turning now to solutions, we have to deal with osmotic pressure instead of gas-pressure. The osmotic pressure is proportional to the amount of dissolved substance, and inversely proportional to the volume. Let u be the mass of the undissociated electrolyte, and u_1 the mass of the dissociated products, and v the volume of the solution:

$$p = \frac{u}{v};\ p_1 = \frac{u_1}{v}.$$

Substituting these values in equation (1), we have —

$$\frac{uv}{u_1^2} = \text{const.} \tag{2}$$

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[1] Planck: *Wied. Ann.* **34**, 139 (1888).

[2] *Ztschr. phys. Chem.* **2**, 36 (1888). *Lehrb. d. Allg. Chem.* (1st edition), II, 723.

We have seen, however, that the amount of dissociation u_1 (or α) is measured by the relation between the conductivity at the given volume v, and at infinite dilution: —

$$u_1 = \frac{\mu_v}{\mu_\infty}.$$

The amount of undissociated substance $u = 1 - \frac{\mu_v}{\mu_\infty}$. Substituting these values for u and u_1 in equation (2), we have —

$$\frac{\mu_\infty\ (\mu_\infty - \mu_v)}{\mu_v^2} v = \text{const.} \tag{3}$$

This expression can be simplified by writing $\alpha = \frac{\mu_v}{\mu_\infty}$, when we have —

$$\frac{\alpha^2}{(1 - \alpha)\, v} = \text{const.}$$

This expression is known as the Ostwald dilution law.

Testing the Ostwald Dilution Law. — Ostwald[1] tested his law by applying it to a large number of substances. He determined the conductivity of a number of solutions of any given substance, and from these results calculated the dissociation at the different dilutions. He then substituted the value of α for any given value of v, in the equation expressing his law, to see whether the result came out a constant over any wide range of dilution. v is the volume of the solution, or number of litres which contain a gram-molecular weight of the electrolyte. The results for two organic acids are given below: —

FORMIC ACID

v	α	CONST. × 100
8	4.05	0.0214
16	6.63	0.0210
32	7.79	0.0206
64	10.78	0.0203
128	14.76	0.0200
256	20.12	0.0198
512	27.10	0.0197
1024	35.80	0.0195

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[1] *Ztschr. phys. Chem.* **3**, 170, 241, 369 (1889).

BUTYRIC ACID

v	α	Const. × 100
8	1.068	0.00144
16	1.536	0.00150
32	2.165	0.00149
64	3.053	0.00150
128	4.292	0.00150
256	5.988	0.00149
512	8.300	0.00147
1024	11.410	0.00144

The results show that the value comes out very nearly a constant. In a word, the Ostwald law holds with fair approximation for this class of substances. The law was applied to between 200 and 300 organic acids, and was found to hold approximately for this class of substances. These organic acids all belong to the weakly dissociated substances. The law was tested for the weakly dissociated organic bases by Bredig.[1] The results for two substances are given. He applied the law to about thirty weak bases.

AMMONIA

v	α	Const. × 100
8	1.35	0.0023
16	1.88	0.0023
32	2.65	0.0023
64	3.76	0.0023
128	5.33	0.0023
256	7.54	0.0024

TRIMETHYLAMINE

v	α	Const. × 100
8	2.31	0.0069
16	3.36	0.0073
32	4.77	0.0075
64	6.73	0.0076
128	9.35	0.0075

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[1] *Ztschr. phys. Chem.* **13**, 289 (1894).

The values found by Bredig for the weak bases are rather nearer a constant than those found by Ostwald for the weak acids. The weak organic bases, like the weak organic acids, belong to the general class of weakly dissociated compounds. The law of Ostwald evidently applies to such substances.

When we turn to the strongly dissociated substances, such as the strong acids and strong bases, and salts, the dilution law of Ostwald does not apply at all satisfactorily. The values found are not at all constant over any considerable range of dilution, but vary greatly with the dilution. No satisfactory reason has yet been furnished, which explains why the law of Ostwald holds for weakly dissociated substances, but does not hold for the strongly dissociated electrolytes. Another, purely empirical expression has, however, been discovered, which applies as well to the strongly dissociated compounds as that of Ostwald to the weak acids and bases.

The Dilution Law of Rudolphi. — The dilution law which was found to hold for the strongly dissociated electrolytes was discovered by Rudolphi.[1] In attempting to apply the Ostwald law to solutions of silver nitrate, he made the following observation: If we represent the volumes of the solution by v, and the constant by c, we obtain from the Ostwald formula: —

$$v = 16, \quad c = 0.26;$$
$$v = 64, \quad c = 0.13;$$
$$v = 256, \quad c = 0.065.$$

A glance at these figures will show that a constant would be obtained, if the values of c were multiplied by the square root of v in each case: —

$$0.26 \times \sqrt{16} = 0.13 \times \sqrt{64} = 0.065 \times \sqrt{256}.$$

Rudolphi substituted for v in the Ostwald equation the square root of v, and obtained —

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = \text{const.}$$

He applied this equation to between fifty and sixty strongly dissociated compounds, and the values found for c always approached closely to a constant. The results for a few substances will be given.

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[1] *Ztschr. phys. Chem.* **17**, 385 (1895).

Hydrochloric Acid		Potassium Sulphite		Potassium Acetate	
v	c	v	c	v	c
2	4.36	2	0.453	2	1.24
4	4.45	8	0.454	100	1.19
8	5.13	32	0.455	1000	1.18
16	5.13	128	0.514	10000	1.03

Although considerable deviations from a constant exist in some cases, yet the law of Rudolphi holds about as well for the strongly dissociated electrolytes as that of Ostwald for the weakly dissociated substances.

The physical significance of the $\sqrt{v}$ in the Rudolphi equation is at present entirely unexplained.

Several further modifications of the dilution laws have been proposed,[1] but they can scarcely be regarded as advances on those already considered. We thus seem to have two expressions for the relation between the dissociation of electrolytes and the dilution of the solutions; the expression of Ostwald, which has a rational basis, and whose physical significance is known, holding for the weakly dissociated compounds; and the purely empirical equation of Rudolphi, which holds for the more strongly dissociated electrolytes. The relation between gaseous and electrolytic dissociation is, then, established as far as the less strongly dissociated compounds are concerned, but when the dissociation is nearly complete at moderate dilutions, there exists a discrepancy which still remains to be explained.

The Conductivity of Organic Acids and the Determination of Dissociation Constants. — The conductivities of from two to three hundred of the more common organic acids have been measured by Ostwald,[2] at dilutions ranging from a few litres to two or three thousand litres. The general fact established by this work is that this whole class of substances is comparatively weakly dissociated even at dilutions of one thousand litres. It is true that they show marked differences in the degree of their dissociation, but few of them are sufficiently dissociated to determine the value of μ_∞ directly by the conductivity method. The indirect method,[3] using the sodium salt, was employed. Knowing the value of μ_∞ for the acid, the dissociation at any dilution could be calculated from the molecular conductivity at that dilution. Knowing the dissociation, the dissociation constant for the acid was calculated from the dilution law, —

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[1] Van't Hoff: *Ztschr. phys. Chem.* **18**, 300 (1895). Kohlrausch: *Ibid.* **18**, 662 (1895). Bancroft: *Ibid.* **31**, 188 (1899).

[2] *Ibid.* **3**, 170, 241, 369 (1889).

[3] *Ibid.* **2**, 840 (1888).

$$\frac{\alpha^2}{(1-\alpha)v} = c.$$

The value of c for different dilutions, which in most cases is fairly constant, gives us a deep insight into the nature of the compound. Knowing its value, we know the relative strength of the acid, with all that is implied by this term.

The effect of replacing hydrogen by different groups was studied by Ostwald, and the influence of constitution as well as composition on the acidity was determined in a number of cases. Thus, the introduction of a halogen, sulphur, or oxygen atom, or the nitro group, increased the acidity. The presence of the amido group diminished it. The presence of oxygen or the nitro group in the ortho position has a greater influence than in the meta position, and in the meta position a greater influence than in the para. For further details reference must be had to the tabulated statement which has been prepared by Ostwald.[1]

Basicity of an Acid determined empirically from its Conductivity. — An empirical relation between the rate of increase in the conductivity of the sodium salts of acids with increase in dilution, and the basicity of the acids was discovered by Ostwald.[2] If we subtract the molecular conductivity of the sodium salt at a dilution containing a gram-molecular weight in 32 l., from its molecular conductivity at a dilution of 1024 l., the difference will be about 10 for monobasic acids, 20 for dibasic, etc. Or if we represent the basicity of the acid by b, the molecular conductivity at 1024 l., minus the molecular conductivity at 32 l., $= 10\,b$: —

$$\mu_{1024} - \mu_{32} = 10\,b.$$

These determinations of conductivity were made at 25°.

A few examples from the work of Ostwald,[3] on acids whose basicity varies from one to five will make this point clear.

Sodium Nicotinate (monobasic)

v	μ_v	
32	68.4	
1024	78.8	
	10.4	difference = 10 × 1

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[1] *Ztschr. phys. Chem.* **3**, 418 (1889). [2] *Ibid.* **1**, 105 (1887); **2**, 902 (1888).
[3] *Ibid.* **2**, 901 (1888).

Sodium Quinolinate (dibasic)

v	μ_v	
32	69.2	
1024	90.0	
	20.8	difference = 10 × 2

Sodium Pyridinetricarbonate (tribasic)

v	μ_v	
32	82.1	
1024	113.1	
	31.0	difference = 10 × 3

Sodium Pyridinetetracarbonate (tetrabasic)

v	μ_v	
32	80.8	
1024	121.2	
	40.4	difference = 10 × 4

Sodium Pyridinepentacarbonate (pentabasic)

v	μ_v	
32	77.7	
1024	127.8	
	50.1	difference = 10 × 5

The extension of this empirical relation to acids more complex than pentabasic cannot be made. Walden[1] has shown that many exceptions exist when the supposed relation is applied to acids of higher basicity.

The Determination of the Conductivity of Organic Bases and their Dissociation Constants. — An elaborate piece of work on the conductivity of organic bases was carried out in the laboratory of Ostwald by Bredig.[2] From his measurements the dissociation constants of these substances were calculated, as in the case of the organic acids, by means of the Ostwald dilution law. The substances studied by Bredig include a large number of substituted ammonias, — primary, secondary, tertiary, and quaternary, the aromatic amines, and a number of other organic and a few inorganic bases. The quaternary amines are by far the strongest, approaching in strength the strongest alkalies. The secondary amines have a larger dissociation constant than either the primary or tertiary, and the primary and tertiary amines are much more strongly dissociated than ammonia itself.

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[1] *Ztschr. phys. Chem.* **1**, 529 (1887); **2**, 49 (1888).

[2] *Ibid.* **13**, 289 (1894).

The effect of constitution on the strength of bases is seen when isomeric substances are compared. As with organic acids so with organic bases, constitution has a marked influence on the strength.

The conductivity of salts of a large number of organic bases was also measured by Bredig.

Migration Velocities of the Complex Organic Anions. — We have seen from the law of Kohlrausch that the conductivity method can be used to determine the velocities of ions. The value of μ_∞ for a compound is the sum of the migration velocities of the two ions. If the value of μ_∞ for the sodium salt of an organic acid is determined, and the velocity constant for sodium subtracted, the remainder is the migration velocity of the anion of the acid. Extensive application has been made of the conductivity method for determining the migration velocity of organic anions, and, as we shall also see, of organic cations.

Ostwald[1] has arrived at general conclusions from his measurements as to the effect both of composition and constitution of the ion on its velocity. The effect of increasing complexity is illustrated by the following example: —

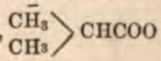
	Velocity
Anion of formic acid, $\mathrm{H\overset{-}{C}OO}$	55.9
Anion of acetic acid, $\mathrm{C\overset{-}{H}_3COO}$	43.1
Anion of propionic acid, $\mathrm{CH_3C\overset{-}{H}_2COO}$	39.0

It is obvious that as the ion becomes more complex its velocity becomes smaller.

When hydrogen is replaced by chlorine the velocity becomes less, as is shown by the following example: —

	Velocity
Anion of acetic acid, $\mathrm{C\overset{-}{H}_3COO}$	43.1
Anion of monochloracetic acid, $\mathrm{CH_2\overset{-}{Cl}COO}$	42.0
Anion of dichloracetic acid, $\mathrm{CH\overset{-}{Cl}_2COO}$	40.1
Anion of trichloracetic acid, $\mathrm{CCl_3COO}$	37.5

The effect of constitution on migration velocity was studied with isomeric ions. The following results show that isomeric ions move with very nearly the same velocity: —

	Velocity
Anion of butyric acid, $\mathrm{CH_3\overset{-}{CH_2}CH_2COO}$	35.4
Anion of isobutyric acid,  $\mathrm{\begin{matrix}\overset{-}{CH_3}\\ CH_3\end{matrix}\!\!>CHCOO}$	35.6

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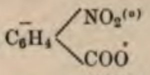
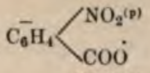
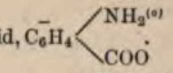
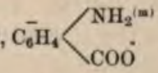
[1] *Ztschr. phys. Chem.* **2**, 848 (1888).

	VELOCITY
Anion of orthonitrobenzoic acid,  $\overset{-}{C_6H_4}<\begin{matrix}NO_2^{(o)}\\ \overset{\cdot}{COO}\end{matrix}$	34.5
Anion of paranitrobenzoic acid,  $\overset{-}{C_6H_4}<\begin{matrix}NO_2^{(p)}\\ \overset{\cdot}{COO}\end{matrix}$	34.8
Anion of orthoamidobenzoic acid,  $\overset{-}{C_6H_4}<\begin{matrix}NH_2^{(o)}\\ \overset{\cdot}{COO}\end{matrix}$	35.7
Anion of metaamidobenzoic acid,  $\overset{-}{C_6H_4}<\begin{matrix}NH_2^{(m)}\\ \overset{\cdot}{COO}\end{matrix}$	34.6

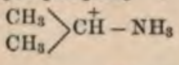
Other relations were pointed out by Ostwald for the organic anions, but for these his original paper must be consulted.

Migration Velocities of the Complex Organic Cations. — The velocities of many organic cations were calculated from the conductivities of salts of the organic bases by a method strictly analogous to that already discussed for the anions of organic acids. The value of μ_∞ for a salt of the base was determined directly by the conductivity method, the velocity of the anion of the salt subtracted, and the remainder, from the law of Kohlrausch, is the velocity of the cation. Some of the relations which obtain for the cations are similar to those already pointed out for the anions. A few of these will be referred to, but for a full discussion of this subject reference must be made to the elaborate investigation of Bredig.[1]

The more complex the cation, the slower its velocity.

	VELOCITY
Ammonium, $\overset{+}{N}H_4$	70.4
Methylammonium, $CH_3\overset{+}{N}H_3$	57.6
Ethylammonium, $C_2H_5\overset{+}{N}H_3$	46.8

Isomeric ions which have analogous constitution have approximately the same velocities.

	VELOCITY
Propylammonium, $CH_3C\overset{+}{H_2}CH_2NH_3$	40.1
Isopropylammonium,  $\begin{matrix}CH_3\\ CH_3\end{matrix}>C\overset{+}{H}-NH_3$	40.0

If they differ greatly in constitution, isomeric ions usually have different velocities.

	VELOCITY
Trimethylpropylammonium, $(CH_3)_3C_3H_7N$	36.2
Dimethyldiethylammonium, $(CH_3)_2(C_2H_5)_2N$	38.2

The effect of constitution may in some cases overcome that of composition, and the more complex ion move the faster.

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[1] *Loc. cit.*

	VELOCITY
Methyldiethylammonium, $CH_3(\overset{+}{C}_2H_5)_2NH$	35.8
Dimethyldiethylammonium $(CH_3)_2\,(\overset{+}{C}_2H_5)_2N$	38.2

This last example serves also to illustrate another fact. The more symmetrical the substitution or the more symmetrical the ion, the swifter its movement. The second ion, although more complex than the first, is more symmetrical and has a greater velocity.

Effect of Pressure on the Conductivity of Solutions. — The effect of pressure on the conductivity of solutions was studied by Fanjung.[1] The pressure was produced by means of a Cailletet pump. We should expect that whatever the effect of pressure on the amount of dissociation of the compound, it would increase the friction on the ions as they move through the electrolyte, and consequently diminish the conductivity. The fact is, the conductivity is increased by pressure.

This is shown by the following example: —

	ATMOSPHERES PRESSURE	MOLECULAR CONDUCT μ_v
Acetic Acid Normal Solution	1	1.38
	42	1.39
	91	1.42
	138	1.44
	182	1.46
	224	1.48
	260	1.50

Since conductivity is conditioned both by the number of ions present and the velocity with which they move through the solution, an increase in conductivity may be due to either of two causes, an increase in the amount of dissociation, or an increase in the velocity with which the ions move. To determine which of these influences was at work, Fanjung took solutions which were so dilute that they were completely dissociated, and studied the effect of pressure on their conductivity. In these cases the conductivity was increased by pressure.

It is obvious that in all such cases the effect of pressure is not to increase the dissociation, since it is complete at ordinary pressure. The increase in the conductivity must, therefore, be due to an increase in the velocity with which the ions move.

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[1] *Ztschr. phys. Chem.* **14**, 673 (1894).

By comparing the amount of increase in conductivity with pressure, in the case of completely dissociated solutions, with the increase in the conductivity with pressure when the dissociation is not complete, we seem to be justified in concluding that the effect of pressure in all cases is to increase the velocity of the ions and not their number.

Isohydric Solutions. — If we mix two solutions of electrolytes, the conductivity of the mixture is not in general the mean of the conductivities of the constituents, but is usually less. There are, however, concentrations at which solutions of electrolytes can be mixed without affecting each other's conductivities. This fact was known, but no satisfactory explanation was offered until the problem was taken up by Arrhenius.[1] He worked with acids, and showed that when a solution of an acid is mixed with a solution of another acid of a certain concentration, the conductivity of the mixture is the mean of the conductivities of the two solutions. Such solutions Arrhenius termed *isohydric*. They are defined by him[2] as follows: —

"Two solutions of acids are isohydric whose conductivity, or, in other words, whose electrolytic dissociation is not changed if they are mixed."

The conditions which must be fulfilled in order that two solutions containing a common ion may be isohydric, have been worked out by Arrhenius,[2] assuming that each electrolyte is partly dissociated into ions: —

"Given two acids H_mA and H_nB, dissolved in water, the volumes of the solutions being respectively V_a and V_b. Of the acid H_mA let a gram-molecules be undissociated, and α gram-molecules dissociated into the ions mH and A. Let the corresponding symbols for the acid H_nB, be b and β.

"In consequence of the analogy between matter in very dilute solution and in the gaseous condition, recognized by Van't Hoff, the following equations hold for the original solutions: —

$$K_a \frac{a}{V_a} = \frac{(m\alpha)^m}{V_a{}^m} \cdot \frac{\alpha}{V_a} \tag{1}$$

and

$$K_b \frac{b}{V_b} = \frac{(n\beta)^n}{V_b{}^n} \cdot \frac{\beta}{V_b}, \tag{1a}$$

where K_a and K_b are two constants independent of the values a, α, V_a and b, β, V_b.

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[1] *Wied. Ann.* **30**, 51 (1887).

[2] *Ztschr. phys. Chem.* **2**, 284 (1888).

"These equations express the existence of equilibrium between the concentrations of the undissociated parts $\left(\frac{a}{V_a} \text{ and } \frac{b}{V_b}\right)$, and the concentrations of the ions $\left(\frac{m\alpha}{V_a} \text{ and } \frac{\alpha}{V_a};\ \frac{n\beta}{V_b} \text{ and } \frac{\beta}{V_b}\right)$. If the solutions are isohydric, the dissociated part (α), and consequently the undissociated part (a), will undergo no change on mixing. If the solutions are sufficiently dilute, the volume after the mixing will be $V_a + V_b$, and the number of hydrogen ions $(m\alpha + n\beta)$. Therefore, we have the following equations:—

$$K_a \frac{a}{(V_a + V_b)} = \left(\frac{m\alpha + n\beta}{V_a + V_b}\right)^m \cdot \frac{\alpha}{V_a + V_b}; \tag{2}$$

$$K_b \frac{b}{V_a + V_b} = \left(\frac{m\alpha + n\beta}{V_a + V_b}\right)^n \cdot \frac{\beta}{V_a + V_b}. \tag{2a}$$

"From (1) and (2) we have:

$$\frac{m\alpha + n\beta}{V_a + V_b} = \frac{m\alpha}{V_a}, \tag{3}$$

and from (1a) and (2a)

$$\frac{m\alpha + n\beta}{V_a + V_b} = \frac{n\beta}{V_b}. \tag{3a}$$

"These two equations lead to the same result, viz., that

$$\frac{m\alpha}{V_a} = \frac{n\beta}{V_b}. \tag{4}$$

"The fact that these two equations give the same solution, shows that if the electrolytic dissociation of the solution of the one acid is not changed by mixing the two solutions, the same holds for the dissociation of the other solution."

As Arrhenius points out, equation (4) also shows that solutions of two acids are isohydric if they contain in unit volume the same number of hydrogen ions. And, further, that two solutions are isohydric if they have certain definite concentrations, and, therefore, this is independent of the amount of either solution mixed with the other. Isohydric solutions can be mixed in any proportion without destroying their isohydric nature.

The discovery of the nature of isohydric solutions is of considerable importance in physical chemistry. It comes into play especially in connection with problems in chemical equilibrium, and the conditions which must be fulfilled in order that equilibrium may exist.

The Condition of Double Salts in Solution. — One other application of the conductivity method to aqueous solutions must be considered before this section is closed. The question as to the condition of double salts in solution has been repeatedly the object of investigation. Do double salts like the alums, double halides, etc., break down in water into their constituent salts, and then these constituents undergo dissociation as if they were alone, or do the double salts dissociate as if they were salts of complex acids? This difference can be made clear by the following example. Does the compound K_2CdI_4 break down into $2\,KI$ and CdI_2, and then these undergo electrolytic dissociation into their ions, or does it dissociate at once into $\overset{+}{K} + \overset{+}{K} + \overset{=}{CdI_4}$?

This can be decided by the conductivity method. If they break down as first suggested, the conductivity of the double salt would be the sum of the conductivities of the constituents at the same concentration, less, of course, the effect of each salt on the dissociation of the other due to the fact that the solutions are not isohydric.

If they dissociate as salts of complex acids, the conductivity of the double salt would be much less than the sum of the conductivities of the constituents, since the number of ions in the solution would be much less. Among those who have applied the conductivity method to this problem are Grotrian,[1] Arrhenius,[2] Klein,[3] and Kistiakowsky.[4] Four investigations on this problem have been carried out recently in this laboratory by Mackay,[5] Ota,[6] Knight,[7] and Caldwell.[8] The general result obtained is that double salts break down in concentrated aqueous solution to some extent as if they were salts of complex acids. As the dilution increases the complex ions break down more and more, until at very great dilution they are completely dissociated into the simplest possible ions, just like their constituents. The effect due to the solutions not being isohydric is determined by studying mixtures of salts which cannot combine and form double salts.

The Conductivity of Fused Electrolytes. — We have seen that aqueous solutions of acids, bases, and salts conduct the current to a greater or less extent, and are, therefore, electrolytes. The question remains whether the substances would conduct under any conditions in the pure state, if there was no water present? if they do not conduct in the solid state, would they conduct when fused? This has been repeatedly investigated. The work of Poincaré[1] and Bouty[2] on this problem is very important. They devised a special method and applied it to a large number of fused salts. They determined the specific conductivities and also calculated the molecular conductivities in a number of cases, knowing the specific and molecular volumes of the fused salts. A few results are given, the molecular conductivities being expressed in reciprocal ohms, to show the order of magnitude of the conductivity of fused salts.

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[1] *Wied. Ann.* **18**, 177 (1883).

[2] *Ibid.* **30**, 51 (1887).

[3] *Ibid.* **27**, 151 (1886).

[4] *Ztschr. phys. Chem.* **6**, 97 (1890).

[5] *Amer. Chem. Journ.* **19**, 83 (1897).

[6] *Ibid.* **22**, 5 (1899).

[7] *Ibid.* **22**, 110 (1899).

[8] *Ibid.* **25**, 349 (1901).

	TEMP.	μ		TEMP.	μ
KNO_3	350°	39.7	$CaCl_2$	750°	58.8
$AgNO_3$	350°	60.2	KBr	750°	79.4
NH_4NO_3	200°	23.3	KI	650°	73.8
NaCl	750°	120.6	NaI	650°	130.1

These results show that heat as well as water can dissociate electrolytes to a very considerable extent.

In connection with the conductivity of fused electrolytes we should mention also the work of Graetz.[3] He found a very marked conductivity for the halogen compounds of cadmium, zinc, lead, copper, and tin. He studied their conductivities below their melting-points, and found that the solid substances at high temperatures showed very marked conductivity. With certain salts this increased regularly up to and through the melting-point. With others the increase is very rapid near and at the melting-point.

W. Kohlrausch[4] showed that the halogen salts of silver have a marked conductivity long before the melting-point is reached. The chloride and bromide show regular conductivity up to and through the melting-point, but the conductivity increases rapidly with temperature after the salt has fused. Silver iodide behaves abnormally; its conductivity increases slowly with increasing temperature above the melting-point, but for a long distance below the melting-point the conductivity decreases very slowly. The conductivity does not decrease rapidly until a temperature as low as 160° is reached.

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[1] *Ann. Chim. Phys.* [6], **17**, 52 (1889).

[2] *Ibid.* **6**, 21, 289 (1890).

[3] *Wied. Ann.* **40**, 18 (1890).

[4] *Ibid.* **17**, 642 (1882).

DISSOCIATING ACTION OF WATER AND OTHER SOLVENTS

Demonstration of the Presence of Free Ions in Solution. — As our subject has developed, we have studied a number of lines of evidence bearing upon the theory of electrolytic dissociation. In nearly every case the correctness of the theory as expressing a great general truth of nature has been established. This large body of evidence would, however, be greatly strengthened if some direct demonstration of the presence of free ions in solution could be furnished. This has been done by Ostwald and Nernst.[1] Their experiment is as follows: —

A glass tube 30 to 40 cm. in length, provided with a stopcock, was drawn out at one end to a fine capillary. The diameter of the capillary was such that when the tube was filled with mercury, it would begin to flow out of the fine point. The tube was fastened upright, and its tip allowed to dip in dilute sulphuric acid. The mercury was then drawn up into the capillary, and the acid drawn in after it. By means of the stopcock, the surface of contact between the mercury and the acid could be kept about the middle of the capillary. A platinum wire fused into the glass tube connected with the mercury.

A large glass flask was filled with dilute sulphuric acid. Its outer surface was covered with tinfoil, and its neck varnished with shellac. The contents of the flask were connected with the sulphuric acid into which the capillary tube dipped, by means of a moist cord. The glass flask was insulated, by placing it upon a plate of hard rubber. The outer coating on the flask was connected with the positive pole of a small machine for generating electricity; the mercury in the tube connected with the earth. When the machine was set in motion, the meniscus in the capillary rushed up with violence, and at the same time several bubbles of gas separated, which broke the thread of mercury in a number of places. This is nearly the verbatim account of what happened, as given by the experimenters themselves.

They explain the facts as follows: "By charging the coating on the outside of the flask with positive electricity, the negative electricity in the interior is attracted and held, while the positive is repelled. The latter passes through the thread into the capillary electrode, and through the platinum wire in the latter to the earth. There is no closed current present; the entire movement of electricity which is produced is the result of induction."[2]

As the outer coating of the flask becomes charged with positive electricity, the ions, SO_4, which carry the negative charge, are attracted, the positive ions, hydrogen, are repelled, pass over the moist cord to the mercury, give up their charge, and appear as ordinary hydrogen gas.

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[1] *Ztschr. phys. Chem.* **3**, 120 (1889).

[2] *Ibid.* **3**, 122 (1889).

The objection could be raised to this experiment, that a movement of electricity takes place, electrolytically, through the glass, and that this causes the separation of the hydrogen. The authors performed a number of experiments to test this point, and convinced themselves that this is strictly an induction phenomenon.

They worked quantitatively, as far as possible, determining the amount of hydrogen which separates and the amount of the electricity induced, and found that the amount of gas liberated corresponded to that calculated from Faraday's law to within the limit of experimental error. They concluded that movement of electricity in electrolytes, corresponding to Faraday's law, can take place only with a simultaneous movement of the ions, and that in electrostatically charged electrolytes a number of ions, corresponding to the amount of electricity, are free.

The question still remains, whether the ions are not set free at the moment of the electrostatic charging of the tinfoil, so that the separation of the electricities is accompanied by a kind of electrolysis in the interior of the liquid. Ostwald and Nernst point out that Clausius has shown that the movement of electricity in electrolytes obeys the weakest electromotive impulses, which would not be possible if the electricity must first perform an appreciable amount of work. They then show that such an assumption is against the laws of thermodynamics.

If we consider all the precautions which Ostwald and Nernst have taken, it seems that they have conclusively proved the point, that free ions exist in electrostatically charged electrolytes, and that these are not set free at the moment of charging.

Modes of Ion Formation. — From what has been said thus far, the impression might be gained that ions can be formed from molecules in only one way — the molecules breaking down directly into an equivalent number of anions and cations. This is one way in which ions are formed, and the way with which we are most familiar, since it occurs most frequently. The following examples illustrate this mode of ion formation: —

1. $$HCl = \overset{+}{H} + \overset{-}{Cl}, \qquad H_2SO_4 = \overset{+}{H} + \overset{+}{H} + \overset{=}{SO_4},$$
$$NaOH = \overset{+}{Na} + \overset{-}{OH}, \quad Ba(OH)_2 = \overset{++}{Ba} + \overset{-}{OH} + \overset{-}{OH},$$
$$KNO_3 = \overset{+}{K} + \overset{-}{NO_3}, \qquad K_2SO_4 = \overset{+}{K} + \overset{+}{K} + \overset{=}{SO_4}.$$

Another method by which an ion can be formed is for an atom to take the charge from an ion, converting it into an atom — the original ion becoming an atom. Thus, when a bar of zinc is dipped into a solution of copper salt, the copper which was present in the solution as an ion gives up its two charges to an atom of zinc, becoming an atom; while the zinc, having received the charges, becomes an ion. This is the well-known precipitation of copper from a solution by zinc. We will call this the second mode of ion formation.

2. $$\overset{++}{\mathrm{Cu}} + \overset{=}{\mathrm{SO_4}} + \mathrm{Zn} = \overset{++}{\mathrm{Zn}} + \overset{=}{\mathrm{SO_4}} + \mathrm{Cu}.$$

All that occurs is a transference of electricity from the copper to the zinc. This is exactly analogous to what takes place whenever one metal replaces another, as it is said, from its salts.

Another method of ion formation is where an atom of one substance passes over into a cation, at the same time that an atom of another substance passes over into an anion. When gold is dipped into chlorine water, both the gold and chlorine are in the atomic or molecular condition. But under these conditions the gold can become a cation, and the chlorine can form anions. This we will term the third method of ion formation.

3. $$\mathrm{Au} + \mathrm{Cl} + \mathrm{Cl} + \mathrm{Cl} = \overset{+++}{\mathrm{Au}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}}.$$

This is usually expressed by saying that gold dissolves in chlorine water.

The fourth and last method by which ions are formed is where an atom passes over into an ion, at the same time converting an ion already present into one with a different quantity of electricity upon it. Thus, chlorine brought in contact with ferrous chloride in solution, forms an anion, at the same time converting the ferrous ion into a ferric ion.

4. $$\overset{++}{\mathrm{Fe}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}} + \mathrm{Cl} = \overset{+++}{\mathrm{Fe}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}}.$$

This is an example of what has so frequently been called in chemistry, oxidation. The reverse phenomenon is, of course, what has been termed reduction. In this sense oxidation is simply increasing the number of charges carried by an ion, and reduction is diminishing the number of such charges.

These four methods of ion formation, which have been so clearly pointed out by Ostwald,[1] include all the cases which are known. If we study them carefully and apply them to chemical reactions, we shall see that they throw much light on many problems in chemistry, the meaning of which has hitherto been concealed in darkness.

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[1] See *Lehrb. d. Allg. Chem.* II, 786.

The Dissociating Power of Different Solvents. — Frequent reference has been made to the power of water to dissociate molecules into ions. From this the conclusion might be drawn that water is the only solvent which has this power. Such is not at all the case. Practically all liquids have the power of dissociating strong acids and bases, and salts, when dissolved in them. But they possess this property to a very different degree. We should be familiar with the relative dissociating power of some of the more common solvents.

The same methods are available, at least theoretically, for measuring dissociation in non-aqueous solvents as have been employed with water. These are, as will be remembered, the freezing-point, boiling-point, and conductivity methods. The freezing-point method, however, can be applied to only a few solvents, since the freezing-points of most liquids are either too high or too low to come within the range of this method. The boiling-point method for a long time was not applied to the problem of electrolytic dissociation, because it was not regarded as sufficiently accurate to give results which would have much value. This method has recently been improved[1] and applied to the determination of dissociation in some of the alcohols, with a fair degree of success.

The conductivity method has been used extensively to determine the dissociating power of a large number of solvents, but even with this method a serious difficulty is encountered. In order to measure dissociation by the conductivity method, it is not only necessary to know the molecular conductivity of the solution in question, but the molecular conductivity at complete dissociation. As will be remembered, $\alpha = \frac{\mu_v}{\mu_\infty}$. To determine α, it is necessary to know both μ_v and μ_∞. The great difficulty in applying the conductivity method to measure dissociation in a solvent with small dissociating power, lies in obtaining the value of μ_∞. Unless the solvent has very great dissociating power, the dilution at which the dissolved substance is completely dissociated is so great that the conductivity method cannot be applied to it. To determine the value of μ_∞ in such solvents it is necessary to make some assumption which often has not been proved, and, consequently, the results obtained may be inaccurate to the extent of several per cent. Yet, on the whole, the conductivity method is the best at our disposal for determining approximately the dissociating power of a large number of solvents; and the results obtained by means of it are probably, in most cases, a fair approximation to the truth.

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[1] Jones: *Ztschr. phys. Chem.* (Jubelband zu Van't Hoff), **31**, 114 (1899).

The dissociating power of a few of the more common solvents will be considered a little more in detail. *Water* is the strongest dissociant of any solvent thus far known. Its dissociating power has been determined by Kohlrausch,[1] Ostwald,[2] Bredig,[3] and a large number of other experimenters using the conductivity method; also by Jones,[4] Loomis,[5] and others, working with the freezing-point method.

A little work done by Bouty[6] on *nitric acid* would indicate that its dissociating power is very high, but the data are too few up to the present to say just what is its power to dissociate electrolytes. *Formic acid* has been shown by the work of Zanninovich-Tessarin[7] to have a very strong dissociating action. A comparison with aqueous solutions will show that this solvent dissociates salts to about three-fourths the extent of water.

Methyl alcohol has a stronger dissociating power than any other alcohol. This has been shown by the work of many; but especially by that of Carrara,[8] Völlmer,[9] and Zelinsky and Krapiwin.[10] That it has high dissociating power has been shown also by the work of Jones[11] with the boiling-point method. Its dissociating power is from one-half to two-thirds that of water.

Ethyl alcohol dissociates much less than methyl alcohol, as has been shown by Völlmer,[12] Carrara,[13] Jones,[14] and others. The dissociating power of ethyl alcohol is not more than half that of methyl alcohol.

Ammonia in the liquid state has been shown by Franklin and Kraus[15] to have very high dissociating power, but not as high as was first supposed. It dissociates to about one-third to one-fourth the extent of water.

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[1] *Wied. Ann.* **26**, 161 (1895).

[2] *Ztschr. phys. Chem.* **3**, 170, 241, 369 (1899).

[3] *Ibid.* **13**, 191, 289 (1894).

[4] *Ibid.* **11**, 110, 529; **12**, 623 (1893).

[5] *Wied. Ann.* **51**, 500 (1894); **57**, 495 (1896); **60**, 523 (1897).

[6] *Compt. rend.* **106**, 595 (1888).

[7] *Ztschr. phys. Chem.* **19**, 25 (1896).

[8] *Gazz. chim. ital.* **26**, I, 119 (1896).

[9] *Wied. Ann.* **52**, 328 (1894).

[10] *Ztschr. phys. Chem.* **21**, 35 (1896).

[11] *Ibid.* **31**, 127 (1899).

[12] *Loc. cit.*

[13] *Loc. cit.*

[14] *Loc. cit.*

[15] *Amer. Chem. Journ.* **20**, 820, 838 (1898).

Sulphur dioxide in the liquid condition has very considerable dissociating power, as has been shown by the work of Walden.[1]

Acetone and other ketones have been found by Carrara,[2] Dutoit and Aston,[3] and others, to have considerable dissociating power — acetone effecting ionization to a greater extent than any other ketone. Indeed, it is a general rule that of an homologous series of compounds the lowest member has the highest dissociating power, and this power decreases as the members become more and more complex.

Considerable work has already been done on the dissociating power of many other inorganic and organic solvents. The *hydrocarbons and their substitution products*, the *ethers, aldehydes, ethereal salts*, etc., have very slight dissociating power.

For further details in connection with the dissociating power of solvents reference must be had to a review of all the work which has been done up to the present on non-aqueous solvents, which has just been prepared by Jones.[4]

Abnormal Results obtained in Non-aqueous Solvents. — While the conductivities in non-aqueous solvents follow the same rules, in general, which obtain for aqueous solutions, yet exceptions are not wanting. Thus, it is a general rule in aqueous solutions that the molecular conductivity increases with the dilution of the solution up to a certain point, where it becomes constant. There are several exceptions to this general relation, already discovered in non-aqueous solvents. Kablukoff[5] has shown that the molecular conductivity of hydrochloric acid in ether decreases with increase in the dilution of the solution, and hydrochloric acid dissolved in isoamyl alcohol showed the same phenomenon. On the other hand, hydrochloric acid dissolved in isobutyl alcohol gave perfectly normal results. Jones[6] found results similar to those obtained by Kablukoff with sulphuric acid in acetic acid. The molecular conductivity of the sulphuric acid decreased with increase in the dilution of the solution. The meaning of these results is at present entirely unknown.

Abnormal results of an entirely different character were obtained *in certain mixed solvents*. When Zelinsky and Krapiwin[7] were measuring the conductivities of salts in methyl alcohol, it occurred to them to measure their conductivities also in mixtures of methyl alcohol and water. The conductivities in water are considerably higher than in methyl alcohol under the same conditions of temperature and concentration, so that we would expect the conductivities in a mixture of the two solvents to be higher than in pure methyl alcohol. Exactly the opposite was found. The conductivity in a mixture of 50 per cent alcohol and 50 per cent water was less than in pure methyl alcohol, as will be seen from the following results for potassium bromide. *V* is the volume or number of litres containing a gram-molecular weight of the electrolyte. The molecular conductivities (μ_v) in pure water, in pure methyl alcohol, and in 50 per cent water and 50 per cent alcohol are given in the three columns: —

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[1] *Ber. d. Chem. Gesell.* **32**, 2862 (1899).

[2] *Gazz. chim. ital.* **27**, I, 207 (1897).

[3] *Compt. rend.* **125**, 240 (1894).

[4] *Amer. Chem. Journ.* **25**, 232 (1901).

[5] *Ztschr. phys. Chem.* **4**, 429 (1889).

[6] *Ibid.* **13**, 419 (1894). *Amer. Chem. Journ.* **16**, 1 (1894).

[7] *Ztschr. phys. Chem.* **21**, 35 (1896).

POTASSIUM BROMIDE

	WATER	METHYL ALCOHOL	ONE-HALF WATER AND ONE-HALF METHYL ALCOHOL
v	μ_v	μ_v	μ_v
16	123.1		59.82
32	127.5	69.02	62.46
64	130.5	76.70	65.36
128	132.9	83.60	67.11
256	136.4	88.96	69.26
512	140.2	93.26	70.53
1024	143.4	97.25	

The presence of the water in the methyl alcohol decreases very considerably the conductivity of the dissolved salt. The meaning of this very surprising result is at present also entirely unknown.

Relation between the Dissociating Power and Other Properties of Solvents. — Attempts have been made to discover relations between the dissociating power and other properties of solvents. J. J. Thomson,[1] and a little later Nernst,[2] have pointed out that if the forces which hold the atoms in the molecule are of an electrical nature, those solvents which have the highest dielectric constant should have the greatest dissociating power. The work which has thus far been done shows that this is, in general, true. There is not, however, a proportionality between the dielectric constants and the ionizing power of solvents. The exact relation between the two has not yet been pointed out, nor can we hope to discover it until we can measure dissociation in non-aqueous solvents far more accurately than is possible at present.

[1] *Phil. Mag.* **36**, 320 (1893).

[2] *Ztschr. phys. Chem.* **13**, 531 (1894).

An entirely different relation has been suggested by Dutoit and Aston.[1] It is well known, especially from the work of Ramsay and Shields,[2] that in many liquids the molecules are not the simplest possible, but are aggregates of these simplest molecules of various degrees of complexity — the liquid molecules are polymerizations of the simplest gas molecules. The relation suggested by Dutoit and Aston is that in only those solvents which are polymerized do dissolved substances conduct the current. That there is a relation between the amount of polymerization and the dissociating power of a solvent was shown in a number of cases by Dutoit and Aston, and in a number of other cases by Dutoit and Friderich.[3] The latter concluded that the values of μ_∞ for a given electrolyte in different solvents are a direct function of the degree of polymerization of the solvents, and an inverse function of their coefficients of viscosity. If a solvent is not polymerized at all, its solutions are all non-conductors.

There is undoubtedly some truth in this relation. Water, the strongest dissociant known, represents the highest degree of polymerization of any known liquid. Its molecule, according to Ramsay and Shields, is to be represented by $(H_2O)_4$. Formic acid and methyl alcohol come next in order of polymerization, and as we have seen, they stand next to water in dissociating power. Those substances, on the other hand, which have slight ionizing power show very slight polymerization of their molecules.

Brühl[4] attempts to go one step farther. He thinks that oxygen is generally quadrivalent, and that water and other liquids containing oxygen are unsaturated compounds. This explains according to Brühl their polymerization, their large dielectric constant, and their high dissociating power.

Electrolytic Dissociation and Chemical Activity. — We have seen that most solvents are capable of breaking down to some extent into their ions strong acids and bases, and salts. We have also seen that heat can effect electrolytic dissociation. When we remember that some acid, base, or salt, is used in almost every chemical reaction, we shall see that ions are almost always present whenever chemical action takes place. It is true also that in most chemical reactions molecules are likewise present. These facts would naturally raise the question whether chemical reaction is due directly to the ions or to molecules. We cannot answer this offhand, since under ordinary conditions we have both ions and molecules present. We must, on the one hand, exclude the molecules, having nothing but ions present; and then see whether we have any chemical activity between the ions. On the other hand, we must exclude the ions, having only molecules present, and then see whether we have any chemical activity.

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[1] *Compt. rend.* **125**, 240 (1897).

[2] *Ztschr. phys. Chem.* **12**, 433 (1893).

[3] *Bull. Soc. Chim.* [3], **19**, 321 (1898).

[4] *Ztschr. phys. Chem.* **18**, 514 (1895).

The first part of the problem is solved by working with strong acids and bases, and salts, in very dilute solutions. Under these conditions we know that all the molecules are broken down into ions. We know that it is under just these conditions that the acids, bases, and salts have the *greatest chemical activity.* We do not, of course, mean that a thousandth normal solution of an acid has greater chemical activity than a normal solution, but that it has more than one-thousandth the activity. In a word, the strength of electrolytes increases with the dilution up to a certain point, which represents complete dissociation.

The experimental solution of the second part of the problem is not so simple, because it is difficult to obtain substances which exist entirely in the molecular condition free from ions. This is due chiefly to the difficulty of removing every trace of water from the presence of substances, and wherever water is present we are liable to have molecules dissociated into ions. This has, however, been accomplished in a number of cases, by taking very special precautions to dry the substances themselves, and also the atmosphere around them. Having removed every trace of all dissociating agents, it only remained to bring the molecules of substances into the presence of one another and to see whether they reacted or not. A few of the most striking results which have been obtained will be given.

Wanklyn[1] showed that dry chlorine does not act on fused metallic sodium.

Baker[2] found that sulphur, boron, amorphous and ordinary phosphorus, do not burn in dry oxygen.

Hughes[3] demonstrated that dry hydrochloric acid does not decompose carbonates to any appreciable extent.

Marsh[4] has shown that pure sulphuric acid, free from every trace of moisture, has no action on blue litmus. Similar results have been obtained with dry hydrochloric acid.

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[1] *Chem. News*, **20**, 271 (1869).

[2] *Phil. Trans.* 571 (1888).

[3] *Phil. Mag.* **34**, 117 (1892).

[4] *Chem. News*, **61**, 2 (1890).

Hughes[1] found that dry hydrogen sulphide does not act on dry metallic oxides, and does not precipitate a solution of mercuric chloride in absolute alcohol. It should be stated that mercuric chloride is one of a few salts which is only slightly dissociated by water. It is not dissociated at all by absolute alcohol.

The most astonishing experiments are, however, the following: Hughes[2] stated that when ammonia is dried over lime, and hydrochloric acid is dried over phosphorus pentoxide, the two would remain in the presence of each other for twenty-four hours uncombined. Baker[3] dried both gases very carefully over phosphorus pentoxide, and brought them together in such a form of apparatus that any change in volume, however slight, could be readily observed. He found that perfectly dry ammonia is entirely without action on perfectly dry hydrochloric acid. Although the conclusion of Baker was called in question by Gutmann,[4] it has since been established beyond question by Baker[5] himself.

One other experiment in this connection. An experiment was performed before the Chemical Society of London[6] in which a piece of dry metallic sodium was plunged into pure, dry sulphuric acid. A piece of wire, serving as a handle, was wrapped around the metallic sodium. At first there was a flash of light, then the sodium remained perfectly quiescent in the sulphuric acid. The reaction at first was due to a few ions formed on the surface of the metal by the moisture of the air, to which it was exposed for an instant before it was plunged into the sulphuric acid.

It is needless to add that in all the experiments just described, very special precautions must be taken to dry all the substances in question. The ordinary methods of drying are, of course, entirely insufficient.

These experiments show conclusively that molecules as such have little or no chemical activity, and taken along with the preceding experiments, show that ions are the chief if not the only agents which bring about chemical activity. We have already reached a point where we can say that nearly all, if not all chemical reactions are due to ions, molecules as such not entering into chemical action. The molecules which are present gradually dissociate as the reaction proceeds, and furnish ions which then react.

We can now see why inorganic reactions in general proceed to

[1] *Phil. Mag.* **35**, 531 (1893).

[2] *Loc. cit.*

[3] *Journ. Chem. Soc.* **65**, 611 (1894).

[4] *Lieb. Ann.* **299**, 1, 267 (1898).

[5] *Journ. Chem. Soc.* **73**, 422 (1898).

[6] *Proceed. Chem. Soc.* (1894), p. 86.

the limit rapidly, while organic reactions take place much more slowly. Inorganic compounds, including the strong acids and bases, and salts, are in general strongly dissociated substances. The ions are already present and they react very rapidly. Organic compounds, on the other hand, are weakly dissociated. There are only a few ions present, and considerable time is required, under ordinary conditions, for the dissociation to proceed very far.

ELECTROMOTIVE FORCE OF PRIMARY CELLS

Measurement of Electromotive Force. — Certain forms of apparatus and cells used in measuring electromotive force must be described. More than one form of the *Lippmann electrometer* has been devised. The form described by Le Blanc[1] is very convenient for ordinary purposes. It was devised by Ostwald.

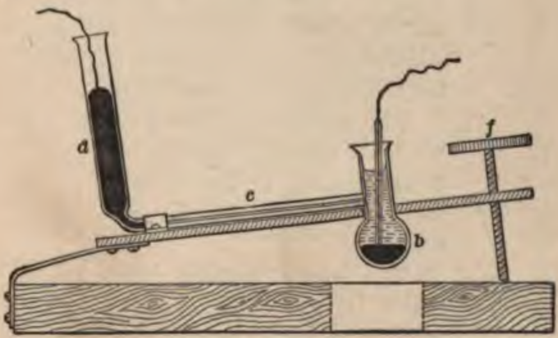

FIG. 47.

The glass tube *d* (Fig. 47) is filled to a convenient height with mercury, which penetrates into the capillary *c*. The bottom of the tube *b* is covered with mercury, and then filled with a ten per cent solution of sulphuric acid, which also penetrates into the capillary *c*. The apparatus is supported on a wooden stand, and the position of the meniscus between the mercury and the sulphuric acid regulated by means of the thumb-screw *f*. A platinum wire, sealed into a glass tube and projecting beyond the sealed end, dips into the mercury in *b*. A platinum wire dips into the mercury in *d*. Beneath the capillary *c* is a scale divided into centimetres and millimetres. If the two platinum wires are brought in contact, the mercury will take a definite position in the capillary, which can be regarded as the zero for the instrument. If the instrument is now thrown into a circuit, there will be a difference in potential between the two wires, and the mercury will be displaced in the capillary in one direction or the other, depending upon the direction of the current. The amount of this displacement, depending upon the difference in the potential of the two wires, is used to measure differences in potential. By this means differences in potential can be measured to a few thousandths of a volt. Ostwald has given the Lippmann electrometer other forms.

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[1] *Ztschr. phys. Chem.* **5**, 471 (1890).

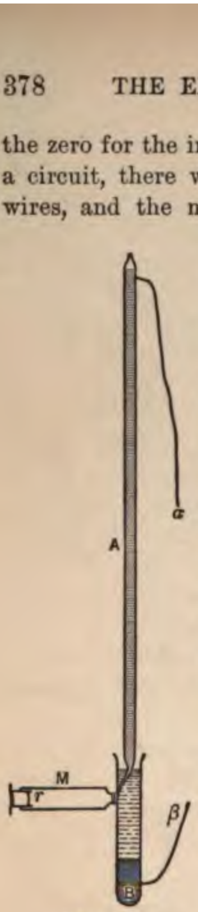

Fig. 48.

The vertical form is very convenient for use with a small microscope, which is employed in reading the scale divisions. A more sensitive form of the Lippmann electrometer is shown in Fig. 48. The capillary is drawn out very fine, and by means of a suitable microscope it is possible to read the differences in potential to a few ten-thousandths of a volt.

The movement of the mercury in the capillary when the current passes is due to the change in the surface-tension produced by the current.

The form of *resistance box*, which is very convenient for measuring the electromotive force of elements, is shown in Fig. 49. On the left side of the box are ten metal plugs connected by wires, each having a resistance of ten ohms. On the right side are ten plugs connected by wires, having a resistance of one hundred ohms each. The two end plugs on this side are connected by a strip of metallic copper, which has practically no resistance. The total resistance of the box is, then, one thousand ohms.

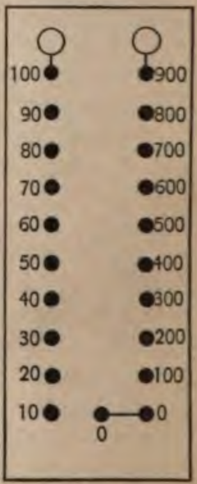

Fig. 49.

A number of *normal elements* have been devised and used. The best known of these is the *Clark* element. It consists of mercury over which is placed a thick paste of mercurous sulphate. Above this is a thick paste of zinc sulphate into which a zinc bar is immersed, serving as the second pole. This element has an electromotive force of 1.4328 volts $- 0.0012\ (t-15°)$,

t being the temperature at which the element is used. The objection to this element is that its temperature coefficient is so large.

The *Weston* element has the advantage that its temperature coefficient is practically zero. It consists of mercury covered with a paste of mercurous sulphate, and above this a paste of cadmium sulphate, into which a bar of cadmium dips. Its electromotive force is 1.0186 volts.

Ostwald[1] recommends the use of a *one volt element* prepared as follows from the Helmholtz calomel element. Mercury is covered with mercurous chloride. Upon this is poured a solution of zinc chloride having the specific gravity 1.409, and into this solution is dipped a bar of amalgamated zinc. Its electromotive force at ordinary temperatures is just one volt, and its temperature coefficient is very small — 0.00007 volt per degree. Such an element must be compared, however, with a standard Clark or Weston element. The *measurement of electromotive force*, by means of the apparatus just described, is comparatively a simple matter. The method consists in balancing the electromotive force of the element in question against that of a standard element. It is known as the *compensation method of Poggendorff.*

This method will be readily understood from Fig. 50. An element of constant electromotive force is placed at *C*, and connected with the two end plugs of the resistance box just described. There is a definite fall in potential as the resistance increases from plug to plug along the box. The element whose electromotive force is to be measured is placed at *E*, and connected with the plugs in the box by means of metallic caps, which fit tightly over the plugs. The caps are moved from plug to plug, until the electromotive force to be

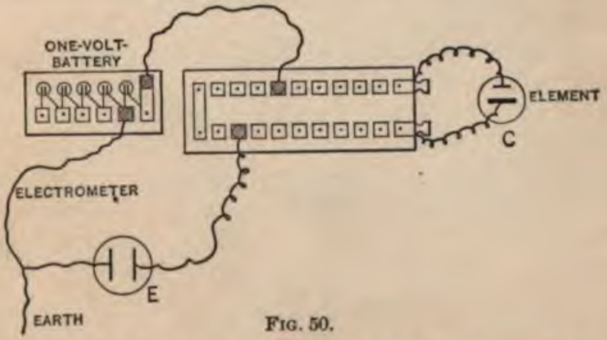

FIG. 50.

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[1] *Ztschr. phys. Chem.* 1, 406 (1887).

measured is equal to the drop in the potential of the original current caused by the resistance in the box. This equality is established by means of the Lippmann electrometer. These two equal values, being opposite in character, completely compensate each other, and there is no movement of the mercury in the electrometer. When larger electromotive forces are to be balanced, one or more one-volt elements may be introduced into the circuit with the element *E*.

It is necessary to determine, for any given element, the drop in potential from plug to plug along the box. This is accomplished by introducing a standard element — say a one-volt element — into the secondary circuit, and moving the caps from plug to plug until the electrometer shows complete compensation. Knowing the electromotive force of the standard element, we know the drop in potential produced by a given resistance in the box, since the two are equal. We can then calculate at once the drop in potential which would be produced when any other resistance was introduced into the path of the current from *C*, by moving the caps along the plugs. It is obvious that the element *C* must have a larger electromotive force than the normal element which is used.

This compensation method has been extensively used in recent years in connection with the large number of measurements of the electromotive force of elements which have been carried out from an electrochemical standpoint.

Transformation of Intrinsic or Chemical Energy into Electrical. — It follows from the law of the conservation of energy, that whenever one form of energy appears, an equivalent amount of some other form disappears. Thus, when electrical energy appears in the cell it is at the expense of the chemical energy of the substances present in the cell. It has already been pointed out that the best means of measuring chemical energy, or better, difference in chemical energy, is to transform this into heat and measure the amount of heat developed, — in a word, to determine the heat tone of the reaction.

The assumption was made by Helmholtz and Kelvin that in the simplest form of cell, the chemical energy which becomes free during the reaction passes over quantitatively into electrical energy. This was shown first by J. Willard Gibbs,[1] in 1878, and a little later by Helmholtz,[2] not to be true in general. Indeed, it is true only in very special cases. An element may either take up heat from the surrounding medium, or give out heat, and this must be taken into account. The electrical energy produced in the cell is, then, equal to the chemical energy which has disappeared, plus a term which is proportional to the electromotive force and to the absolute temperature. This is formulated as follows: If we represent the electrical energy by E_e, the chemical energy by E_c, the quantity of electricity generated in the cell by e_0, the electromotive force by π, and the absolute temperature by T, we have —

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[1] *Proceed. Conn. Acad.* Translated into German by Ostwald: *Thermodynamische Studien*, p. 397. Leipzig, 1892.

[2] *Sitzungsber. Ber. Akad.*, February, 1882.

$$E_e = E_c + e_0 T \frac{d\pi}{dT}.$$

The last term may be either positive or negative, but is more frequently negative; *i.e.* the element gives out heat while it is working. A purely physical chemical method of calculating the electromotive force of elements was worked out by Nernst,[1] and to this we shall now turn.

Calculation of Electromotive Force from Osmotic Pressure. — The method of calculating electromotive force from osmotic pressure is based upon the deduction by Ostwald[2] from the work of Nernst.

If we allow a substance to pass, isothermally, from one condition to another, the maximum amount of external work is always the same, regardless of how this takes place, whether osmotically, or electrically, or in any other way. If we know the maximum external work which is obtainable from a process, we know the amount of electrical energy; and, as we shall see, the electromotive force is calculated directly from the electrical energy. The first step is, then, to determine the maximum external work which is obtainable in a given process. This can be done by allowing the substance to pass at constant temperature, in a reversible manner, from one condition over to the other.

Given a gas under a pressure p_1, and volume v, and allow it to expand isothermally to a pressure p_2. When a gas expands isothermally it takes up heat, and gives it up as volume energy. The energy set free under these conditions is —

$$-\int_{p_1}^{p_2} v dp.$$

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[1] *Ztschr. phys. Chem.* **4**, 128 (1889).

[2] See *Lehrb. d. Allg. Chem.* II, p. 825.

But $pv = RT$, where R is the gas constant and T the absolute temperature, whence the above expression becomes for gram-molecular weights: —

$$-RT\int_{p_1}^{p_2}\frac{dp}{p},$$

which expresses the volume energy obtained under the condition.

This becomes on integration —

$$RT\ln{}^{*}\frac{p_1}{p_2}.$$

This amount of energy, which is converted into work by an ideal gas in passing from pressure p_1 to pressure p_2, is exactly equal to the work obtained from an ideal solution under the same conditions. That is, a solution of volume v passing isothermally from an osmotic pressure p_1 to an osmotic pressure p_2.

But with the movements of the ions, we have the movements of the electrical charges which they carry. And from what has been said, the amounts of work corresponding to the movements of the ions can be transformed into electrical energy.

We have then shown, thus far, how to calculate the maximum external work obtainable, when a solution of osmotic pressure p_1 passes isothermally and reversibly over to osmotic pressure p_2, and the relation between this work and the electrical energy obtainable.

Knowing the electrical energy, how can we determine the electromotive force? Electrical energy, like every other manifestations of energy, can be factored into an intensity and a capacity factor. The intensity factor of electrical energy is the electromotive force or potential, and the capacity factor the amount of electricity. If we call the former π, and the latter e_0, we have the energy electric $E_e = \pi e_0$. If we know E_e, we can calculate π at once, since e_0 is known from Faraday's law. Knowing the quantity of ions which pass from one osmotic pressure over to the other, we know the amount of electricity e_0; knowing E_e, we calculate π.

Let us deal with a gram-molecular weight of univalent ions. These will carry 96,530 coulombs of electricity, and this quantity we will now designate by e_0. If the ions are bivalent, they will carry twice as much; if trivalent, three times; and so on. Let us represent the valence of the ions by v; then a gram-molecular weight will carry ve_0 amount of electricity. Suppose a gram-molecular weight of these ions is charged π potential. The amount of electrical energy required to effect this charge is —

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* ln is natural logarithm.

$$\pi ve_0.$$

But this electrical energy is equal to the osmotic, calculated above, where a gram-molecular weight was taken into account. We have —

$$\pi ve_0 = RT \ln \frac{p_1}{p_2},$$

or,

$$\pi = \frac{RT \ln \frac{p_1}{p_2}}{ve_0}.$$

This is the fundamental equation for calculating the electromotive force of elements, from the osmotic pressures of the electrolytes around the electrodes.

This equation has been very much simplified by Ostwald,[1] by introducing numerical values wherever it is possible.

$R = 2$ calories, and 1 calorie $= 4.18 \times 10^7$ ergs. T, the absolute temperature, can be taken as 290° C. for the average conditions. The constant $\frac{RT}{e_0} = 0.0251$ volt, since volt × coul $= 10^7$ ergs.

The above equation then becomes —

$$\pi = \frac{0.0251}{v} \ln \frac{p_1}{p_2},$$

or in case the ions are univalent —

$$\pi = 0.0251 \ln \frac{p_1}{p_2}.$$

Thus far we have been using the natural logarithm obtained in the process of integration, which we have written ln. It is far more convenient in practice to use the Briggsian. To pass from the former to the latter we must divide the above constant by 0.4343, when we obtain 0.058.

The final expression of the general formula for calculating the electromotive force of an element, from the osmotic pressure of the electrolytes around the electrodes, is then —

$$\pi = 0.058 \log \frac{p_1}{p_2},$$

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[1] See *Lehrb. d. Allg. Chem.* II, p. 827.

where log is the Briggsian logarithm. If the valence of the ion is greater than one, this must be divided by the valence. Before attempting to apply this expression to any concrete cases, we must examine another conception introduced by Nernst.

Electrolytic Solution-tension. — We are perfectly familiar with the fact that when a solid or liquid is evaporated, the molecules pass into the space above the liquid; and equilibrium is established, for a given temperature, when the vapor exerts a certain definite pressure. This pressure is designated as the vapor-tension, or vapor-pressure of the substance in question.

Says Nernst:[1] "If, in accordance with Van't Hoff's theory, we assume that the molecules of a substance in solution exist also under a definite pressure, we must ascribe to a dissolving substance in contact with a solvent, similarly, a power of expansion, for here, also, the molecules are driven into a space in which they exist under a certain pressure. It is evident that every substance will pass into solution until the osmotic partial pressure of the molecules in the solution is equal to the 'solution-tension' of the substance."

Nernst thus introduced the conception of solution-tension; and, at the same time, called attention to the close analogy between evaporation and solution, which can be seen only through a knowledge of the osmotic pressure of solutions. The metals, like many other substances, have the possibility of passing into solution as ions. Every metal in water has, then, a certain solution-tension peculiar to itself, and we will designate this by P.

If we dip a metal into pure water, let us see what will take place. In consequence of the solution-tension of the metal, some ions will pass into solution. When metallic atoms pass over into ions, they must secure positive electricity from something. They take it from the metal itself, which thus becomes negative. The solution becomes positive, because of the positive ions which it has received. At the plane of contact of the metal and solution, there is formed the so-called electrical double layer, whose existence was much earlier recognized by Helmholtz.[2] The positively charged ions in the solution and the negatively charged metal attract one another, and a difference in potential arises. The solution-tension of the metal tends to force more ions into solution, while the electrostatic attraction of the double layer is in opposition to this. Equilibrium is established when these two forces are equal. Since the ions carry such enormous charges, the number which will pass into solution before equilibrium is established is so small that they cannot be detected by any ordinary method. When we are dealing with a metal immersed in pure water, it is evident that the difference in potential which obtains in the double layer is conditioned only by the magnitude of the solution-tension of the metal in question.

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[1] *Ztschr. phys. Chem.* **4**, 150 (1889).

[2] *Wied. Ann.* **7**, 337 (1879).

If we dip a metal of solution-tension P into a solution of one of its salts, the case is not quite as simple. Let the osmotic pressure of the metallic ions in the solution of the salt be p, then either of three conditions may exist. The solution-tension may be greater than the osmotic pressure, less than the osmotic pressure, or just equal to it. We may have —

$$P > p, \tag{1}$$

$$P < p, \tag{2}$$

$$P = p. \tag{3}$$

Let us first take case No. 1, where a metal of solution-tension P is immersed in a solution of one of its salts, in which the osmotic pressure p of the metallic ions is less than its own solution-tension.

At the moment the metal touches the solution, a number of metallic ions, which always carry a positive charge, will pass into solution. These ions have carried positive electricity from the metal into the solution, and the metal has thus become negative, the solution positive. At the places where the metal and solution come in contact, the double layer is formed, due to the attraction of the opposite charges.

"This double layer has a component of force, which acts at right angles to the plane of contact of the metal and solution, and tends to drive back the metallic ions from the electrolytes to the metal. It acts in direct opposition to the electrolytic solution-tension."[1]

The condition of equilibrium is reached when these two opposing forces just equalize one another; and the final result is the existence of an electromotive force between the metal and the solution, the metal being negative, the solution positive.

It is clear that a metal cannot throw as many ions into a solution of its salt as into pure water, because the osmotic pressure of the metallic ions already in the solution acts against the solution-tension of the metal.

Let us now take the second case; where the solution-tension of the metal is less than the osmotic pressure of the metallic ions in the solution. Metallic ions will separate from the solution upon the metal. When a metallic ion passes over into an atom it gives up its positive charge, and in this case it gives it up to the metal, which becomes positive. The solution, having lost some of its positively charged ions, becomes negative. At the points of contact of solution and metal, we have again the electrical double layer, but this time the metal is positive and the solution negative, which is exactly the reverse of the case first considered. Metal ions will separate from the solution until the electrostatic component of force of the double layer, at right angles to the plane of contact of metal and solution, is just equal to the excess of the osmotic pressure over the solution-tension. Equilibrium is established when the sum of the solution-tension of the metal and this component of force is just equal to the osmotic pressure of the metallic ions in the solution. An electromotive force exists here, also, between the metal and the solution, but in the reverse direction from the case first considered.

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[1] *Ztschr. phys. Chem.* **4**, 151 (1889).

The third case is where the solution-tension of the metal is just equal to the osmotic pressure of the metallic ions in the solution. Just as soon as the metal touches the solution, equilibrium is established. Ions neither dissolve from the metal, nor separate from the solution. There is no double electrical layer formed, and there is no difference in potential between the metal and the solution.

If now we inquire which metals have high, and which low, solution-tensions, we shall find that magnesium, zinc, aluminium, cadmium, iron, cobalt, nickel, and the like are always negative when immersed in solutions of their own salts. This means that the solution-tension of the metal is always greater than the osmotic pressure of the metal ion, in any solution of their salts which can be prepared. If, on the other hand, we take gold, silver, mercury, copper, etc., we usually find the metal positive when immersed in a solution of its salt. This means that the solution-tension of the metal is so small, that it is less than the osmotic pressure of the metallic ions in the solution. When a very dilute solution of salts of these metals is prepared, the osmotic pressure of the metallic ions may become less than the very slight solution-tension of these metals; and then the metal would be negative with respect to its solution.

We have, thus far, spoken chiefly of the solution-tension of metals, which tends to drive the metal over into cations. Substances which can pass over into anions have also a solution-tension, as is pointed out by Le Blanc.[1] If the chlorine ions in a solution had an osmotic pressure which was greater than the solution-tension of chlorine, the chlorine ions would pass over into ordinary chlorine. But Le Blanc adds, that, as far as we know, all substances which can yield negative ions have a high solution-tension.

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[1] *Lehrb. Elektrochemie*, p. 121.

Demonstration of the Solution-tension of Metals. — A demonstration of the solution-tension of metals has been furnished by Palmaer.[1] Mercury is a metal whose solution-tension is very small. Even when in contact with a very dilute solution of a mercury salt, the solution-tension of the mercury is less than the osmotic pressure of the mercury ions in the solution; and some of the mercury ions will separate from such a solution.

Given a vessel whose bottom is covered with metallic mercury, and over this is placed a solution of mercurous nitrate having a volume of 2000. A few mercury ions will separate from the solution and give up their positive charges to the mercury. The positively charged mercury will attract electrostatically a few negative NO_3 ions to form the double layer. This will be continued until a certain difference in potential has been reached, when equilibrium will be established. If a drop of mercury is now let fall into the solution, a few mercury ions will separate upon it, charge it positively, and it will then attract an equal number of negative NO_3 ions and drag them down with it through the solution. The next drop of mercury will behave in exactly the same manner, and thus the top of the solution will become continually poorer and poorer in the salt.

When the drop of mercury comes in contact with the mercury at the bottom of the vessel where equilibrium is already established, what will happen? When the drop has united with the mercury, this will contain an excess of positive electricity, and therefore a small quantity of mercury ions will pass into solution. And, indeed, exactly the same number as there are NO_3 ions brought down from the top to the bottom of the solution. The solution will thus become more concentrated just above the layer of mercury on the bottom of the vessel.

A fine glass tube from which mercury flows is known as a drop-electrode. To produce changes in concentration sufficient for the purposes of a demonstration, a very powerful drop-electrode must be used. This is made by inserting a conical glass stopper into a conical glass tube, so that the junction is mercury-tight. A large number of fine grooves are then etched on the outside of the stopper, so that the mercury will stream through as a fine mist. To assist this process the mercury is subjected to four or five atmospheres of pressure.

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[1] *Ztschr. phys. Chem.* **25**, 266 (1898); **28**, 257 (1899). *Ztschr. elek. Chem.* **7**, 287 (1900). See also *Outlines of Electrochemistry*, Jones (Elec. Rev. Pub. Co.).

Under these conditions, however, the mercury cannot be allowed to flow directly into a vessel filled with a dilute solution of a mercury salt, and containing mercury at the bottom, since there would be too much commotion in the solution. The arrangement which was used is shown in Fig. 51. The drop-electrode *T* dips into the funnel-shaped vessel *O*, which is connected by a narrow tube and a rubber tube with the larger vessel *M*. This is in turn connected with the vessel *U*, where the change in concentration can be observed. When the mercury has been allowed to flow for five minutes under a pressure of five atmospheres, distinct changes in concentration can be detected.

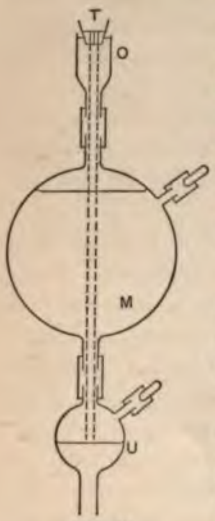

FIG. 51.

Palmaer gives data which show that the concentration above had been diminished as much as fifty per cent, and increased below as much as forty per cent.

This will be recognized at once to be a very remarkable experiment, and before our modern physical chemical theories were proposed would have been entirely inexplicable. The results of this experiment were predicted before the experiment was tried.

Calculation of the Difference in Potential between Metal and Solution. — The difference in potential between a metal of solution-tension *P*, and a solution of one of its salts in which the metal ion has an osmotic pressure *p*, can be calculated as follows: —

When a substance of solution-tension *P* is converted into ions of osmotic pressure *P*, no work is done. Therefore, to convert a substance of solution-tension *P* into ions of osmotic pressure *p*, the maximum work to be obtained is the same as that obtained by transferring the ions from osmotic pressure *P* to osmotic pressure *p*. Now we have seen that the gas laws apply to the osmotic pressure of solutions, and the amount of work can be calculated from a gas in passing from gas-pressure *P* to gas-pressure *p*. If we deal with a gram-molecular weight, we have seen (p. 382) this to be —

$$RT \ln \frac{P}{p}.$$

We have also seen that this osmotic work is equal to the electrical work for an isothermal transformation. The electrical work is the potential times the amount of electricity. If we are dealing with gram-molecular quantities, it is $\pi v e_0$.

Equating these two values, we have —

$$\pi v e_0 = RT \ln \frac{P}{p},$$

or, if the ions are univalent, $v = 1$, when we have —

$$\pi = \frac{RT}{e_0} \ln \frac{P}{p}.$$

Now we know, from page 383, that $\frac{RT}{e_0} = 0.0251$ volt. Passing from natural to Briggsian logarithms, this becomes 0.058 volt.

The potential between metal and solution is then, when $T = 290°$,

$$\pi = 0.058 \log \frac{P}{p}.$$

We have learned thus far how to calculate the electromotive force of elements from the osmotic pressures of the solutions around the electrodes, and also how to calculate the potential between a metal and the solution of one of its salts in which the metal is immersed. With these two conceptions in mind, we will now study a few elements to see how these principles are applied.

Types of Cells. — We know a large number of cells, and they may be classified under the following heads: *Constant* and *Inconstant*, and constant elements may be *reversible* or *non-reversible*.

If the chemical process in the cell remains the same during the time it is closed, the cell is *constant;* if the chemical process changes, it is *inconstant*.

Constant elements differ among themselves. Through some of these we can send a current in the opposite direction, without changing their electromotive force. This class of constant elements is termed *reversible*. This applies to elements in which the electrodes are immersed in solutions of their salts. Take as an example the Daniell element. This consists of a bar of zinc immersed in a solution of zinc sulphate, and a bar of copper in a solution of copper sulphate. When the current is passed in the opposite direction through this cell, its nature is not changed. The normal action is that the zinc dissolves and copper separates. When a current is passed in the opposite direction, copper dissolves and zinc separates. But neither process changes the nature of the cell.

If the electromotive force is changed when a current is passed in the opposite direction, the element is non-reversible.

Concentration Elements of the First Type. — We will first consider a very simple type of a reversible element, the two electrodes being of the same metal, and immersed in solutions of the same salt of that metal, the solutions having different concentrations. To take a concrete example: Two bars of metallic zinc are immersed in solutions of zinc chloride, the one bar in a tenth-normal solution of the salt, the other in a hundredth-normal solution. The two solutions are connected by a tube filled with either solution. When the two zinc bars, which are the electrodes, are connected externally, the current flows and we have an element. Ostwald defines a cell or element as any device in which chemical energy is converted into electrical.

The only difference between the two sides of this element is in the concentration of the electrolytic solutions. The element is therefore termed a "concentration element." Further, since the salt of the metal is *soluble*, this is termed a "concentration element of the first class" to distinguish it from other concentration elements which will be taken up later.

Take the example given above, of two bars of zinc in two solutions of zinc chloride of different concentrations. The action of the cell is such as to make the two solutions become more and more nearly of the same concentration. The more dilute solution becomes more concentrated, and the more concentrated more dilute, until when the two become equal the element ceases to act. Zinc then passes into solution in the more dilute solution, and zinc ions separate as metal on the bar from the more concentrated solution. The electrode in the more concentrated solution is always positive, since metallic ions are giving up their positive charges to it and separating as metal upon it. The electrode in the more dilute solution is negative, because ions are passing from it into the solution, and carrying with them positive charges which come from the electrode. In an element of this kind the current always flows on the outside from the electrode which is immersed in the more concentrated solution.

The action of this cell is just what we would expect. The solution-tension of the zinc is the same on both sides of the cell. The osmotic pressure of the zinc ions is, of course, greater in the more concentrated solution. The osmotic pressure, which works directly against the solution-tension, will cause the ions to separate from the solution in which this pressure is the greater. The electromotive force of such an element would be the difference in the potential upon the two sides of the cell: —

$$\pi = \frac{RT}{ve_0} \ln \frac{P}{p_2} - \frac{RT}{ve_0} \ln \frac{P}{p_1} = \frac{RT}{ve_0} \ln \frac{p_1}{p_2}.$$

Here v is the valence of the cation, p_1 and p_2 the osmotic pressures of the zinc ions in the two solutions. This, however, does not take into account the changes in the concentrations of the solutions, which are taking place while the current is passing.

If e_0 electricity passes from the electrode into the electrolyte, a gram-molecular weight of univalent cations separates from the electrode, dissolves, and increases by unity the concentration around this electrode. But, at the same time, cations are moving from this electrode with the current, over toward the other electrode. The amount depends upon the relative velocities of anion and cation. If we represent the relative velocity of cation by c, and of anion by a, the number of the cations which will move over with the current is $\frac{c}{c+a}$. The increase in the concentration, due to a gram-molecular weight of cations passing into the solution, is then, —

$$1 - \frac{c}{c+a} = \frac{a}{c+a}.$$

This factor is to be multiplied into the former equation to obtain the osmotic work, which can then be equated to its equal, the electrical energy. Let n_i represent the number of ions in the electrolyte. Taking into account both sides of the cell, we have —

$$\pi = \frac{2\,a}{c+a} \frac{n_i RT}{ve_0} \ln \frac{p_1}{p_2};$$

or,

$$\pi = \frac{2\,a}{c+a} \frac{n_i}{v} 0.0002\ T \log \frac{p_1}{p_2}.$$

According to this formula, the only variables are p_1 and p_2, the osmotic pressures of the cation in the two solutions around the electrodes. The electromotive force of such elements should depend only upon the relative osmotic pressures of the solutions, and not upon the absolute osmotic pressures. This has been found to be true. The electromotive force should also be independent of the kind of zinc salt used, provided the salt is soluble, and yields the same number of zinc ions in each solution as the salt in question. Thus the chloride could be replaced by the bromide, iodide, nitrate, etc., of such concentration that the osmotic pressure of the zinc ions remained the same, and the electromotive force of the element should remain unchanged, and again such is the fact. The reason for this will be seen at once by examining the last equation, since it is only the osmotic pressure of the cations which comes into play — the anion having nothing whatever to do with the electromotive force of the element.

The electromotive force of a number of elements of the type we are considering has been measured, and to within the limits which could reasonably be expected has been found to agree with that calculated from the above equation. To calculate the electromotive force, a number of quantities must be measured. c and a, the relative velocities of cation and anion, must be determined; similarly, p_1 and p_2, the osmotic pressures of the cations in the solutions, must be ascertained by indirect methods, which involve the measurement of the dissociation of these solutions. Since each of these processes introduces an error of greater or less magnitude, we could not expect a very close agreement between the electromotive force as measured and as calculated. When we take all of these facts into account the agreement is often surprisingly close.

The following results, obtained by Moser for solutions of copper sulphate with copper electrodes, are cited by Ostwald.[1] The concentrations of solutions I and II are the number of parts of water to one part of copper sulphate. π is the electromotive force expressed in thousandths of a Daniell cell. The unit is 0.0011 volt.

I	II	π OBSERVED	π CALCULATED
128.5	4.208	27	27.4
	6.352	25	23.8
	8.496	21	21.4
	17.07	16	15.8
	34.22	10	10.3

The concentration of one solution was maintained constant throughout, and that of the other varied at will. The agreement in these cases is very satisfactory.

Concentration Elements of the Second Type. — The characteristic of the element which we have just been considering is that the metal is surrounded by one of its soluble salts. We may also have concentration elements in which the metal is surrounded by one of its

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[1] *Lehrb. d. Allg. Chem.* II, p. 833.

insoluble salts; thus, silver surrounded by silver chloride. In the latter case we must have present, in addition, a soluble chloride; and the soluble chloride must be of different concentrations on the two sides of the cell. The element would consist then of a bar of silver, surrounded by solid silver chloride; and over this a solution of some chloride, say potassium chloride; and on the other side, a bar of silver surrounded by solid silver chloride, and over this a solution of potassium chloride, of different concentration from that used on the side first described.

This element is termed a concentration element of the second class.

The action of this cell will be such as to dilute the more concentrated solution of potassium chloride, and to concentrate the more dilute solution. Silver dissolves from the electrode surrounded by the more concentrated potassium chloride, and the ions of silver unite with the chlorine ions, and solid silver chloride is formed. The potassium ions move with the current over to the other side of the element, and form potassium chloride with some of the chlorine which was there in combination with silver as silver chloride. This silver then separates as metal upon the electrode. In this way the more concentrated potassium chloride becomes more dilute, and the more dilute becomes more concentrated.

The electrode immersed in the more concentrated potassium chloride is the one from which silver ions separate; therefore, this is the negative pole. The pole in the more dilute solution of potassium chloride, receiving silver ions, is positive. The current then flows on the outside, from the pole in the more dilute potassium chloride to the pole in the more concentrated.

This is exactly the reverse of what takes place in a concentration element of the first type. There, as we have seen, the current flows on the outside from the pole surrounded by the more concentrated electrolyte.

The electromotive force of a concentration element of the second type is calculated in a manner perfectly analogous to that employed with concentration elements of the first type. The electromotive force π is equal to the difference in the potential at the two poles:—

$$\pi = \frac{RT}{ve_0} \ln \frac{P}{p_2} - \frac{RT}{ve_0} \ln \frac{P}{p_1} = \frac{RT}{ve_0} \ln \frac{p_1}{p_2}.$$

As in the case of the concentration element of the first class, this does not take into account the changes in the concentrations of the electrolytes which are taking place. At the anode the metallic silver is passing into solution, and when e_0 electricity is allowed to flow, a gram-molecular weight of the silver will pass over into ions — will dissolve. This will change the concentration of the potassium chloride around this pole by -1. But at the same time potassium is moving with the current, and chlorine in the opposite direction, and this further changes the concentration. If we represent the relative migration velocities of $\overset{+}{\mathrm{K}}$ and $\overset{-}{\mathrm{Cl}}$, respectively, by c and a, the total change in concentration around the anode will be —

$$-1+\frac{a}{c+a}=-\frac{c}{c+a}.$$

The change in concentration around the cathode would be, of course, —

$$+\frac{c}{c+a}.$$

This factor,

$$-\frac{c}{c+a},$$

must be multiplied into the above expression for electromotive force, when, taking into account the action on both sides of the cell, we have —

$$\pi=-\frac{2\,c}{c+a}\,\frac{n_i RT}{ve_0}\ln\frac{p_1}{p_2};$$

$$\pi=-\frac{2\,c}{c+a}\,\frac{n_i}{v}\,0.0002\ T\log\frac{p_1}{p_2},$$

where n_i is, as before, the number of ions yielded by the electrolyte, and v the valence of the cation. The electromotive force of a number of such elements has been measured by Nernst.[1] Mercury was used as the metal, since it could easily be obtained in pure condition. It was covered with an insoluble salt of mercury, and the soluble electrolyte then added. The chloride, bromide, acetate, and hydroxide of mercury were used, and the soluble electrolyte on both sides of the cell must contain the same anion as the salt of mercury which was employed. If the chloride was used, the soluble electrolyte must be a chloride. If the hydroxide of mercury was employed, a soluble hydroxide must be used, and so on.

Some of the combinations which were made and measured by Nernst are given in the following table. The first column contains the soluble electrolyte which was employed. Columns II and III give the concentrations of the solutions of this electrolyte on the two sides of the cell. "π calculated" is the electromotive force calculated from the preceding formula, and "π found" is the electromotive force of the combination, as measured by Nernst.

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[1] *Ztschr. phys. Chem.* **4**, 159 (1889).

I Soluble Electrolyte	II Concentration 1	III Concentration 2	π Calculated	π Found
HCl	0.105	0.018	0.0717	0.0710
HCl	0.1	0.01	0.0939	0.0926
HBr	0.126	0.0132	0.0917	0.0932
KCl	0.125	0.0125	0.0542	0.0532
NaCl	0.125	0.0125	0.0408	0.0402
LiCl	0.1	0.01	0.0336	0.0354
NH_4Cl	0.1	0.01	0.0531	0.0546
NaBr	0.125	0.0125	0.0404	0.0417
CH_3COONa . . .	0.125	0.0125	0.0604	0.0660
NaOH	0.235	0.030	0.0183	0.0178
KOH	0.1	0.01	0.0298	0.0348
NH_4OH . . .	0.305	0.032	0.0188	0.024

Liquid Elements. — It has long been known that there may be differences in potential at the contact of two solutions of electrolytes. This can be shown by constructing an element in which the two electrodes are of the same metal, and immersed in the same solution of the same electrolyte. There can, therefore, be no difference in potential between the two metals, nor between the metals and electrolytes, for the tensions between the metals and electrolytes are the same on the two sides, and act in direct opposition to one another. If two solutions of electrolytes of different concentrations are introduced into the circuit between the solutions in which the electrodes are immersed, we shall have an element with a certain definite electromotive force. A typical liquid element would be the following: —

Mercury — mercurous chloride.
$\frac{n}{10}$ potassium chloride.
$\frac{n}{100}$ potassium chloride.
$\frac{n}{100}$ hydrochloric acid.
$\frac{n}{10}$ hydrochloric acid.
$\frac{n}{10}$ potassium chloride.
Mercurous chloride — mercury.

Theory of the Liquid Element. — The first satisfactory theory of the liquid element we owe to Nernst.[1] What is the source of the differences in potential in liquid elements? That differences in potential should exist in electrolytes there must be a lack of uniform distribution of ions. The region which is positive must contain an excess of cations, and that which is negative an excess of anions. *The cause of this lack of uniform distribution of ions is to be found in the different velocities with which the different ions diffuse.*

Take the case of a solution of hydrochloric acid in contact with pure water. The hydrogen and chlorine ions in the solution of the acid are present in the same number. They are, therefore, under the same osmotic pressure, and are driven with the same force into the water. But they move with very different velocities, from regions of higher to those of lower osmotic pressure. Hydrogen is, as we have seen, the swiftest of all ions, and moves very much faster than chlorine. It will thus diffuse into the water more rapidly than chlorine, and will tend to separate from the chlorine. But the positive ions cannot separate from the negative ions without producing a separation of the two kinds of electricity. There will result, therefore, electrostatic attractions betweens the layers, which will retard the hydrogen ions and accelerate the chlorine ions, until the two have the same velocity.

Differences in potential will result; and always in the sense that the water or the more dilute solution will have the sign of the swifter ion. Hydrogen being the swiftest of all ions, water or the more dilute solution of acid is always positive with respect to the more concentrated. Next to hydrogen, in order of velocity, comes hydroxyl. Water, or the more dilute solution of a base, must, therefore, always be negative with respect to the more concentrated.

Nernst has shown not only how it is possible to account, qualitatively, for the differences in potential between electrolytes, but has furnished us also with a method of calculating these differences quantitatively.

Given two solutions of different concentrations of an electrolyte like hydrochloric acid, which is composed of a univalent cation and a univalent anion. Let the velocity of the cation be c, and that of the anion a. Let p_1 be the osmotic pressure of both ions in the more concentrated solution, and p_2 the osmotic pressure in the more dilute. If e_0 electricity is passed from the more concentrated to the more dilute solution, $\frac{c}{c+a}$ of a gram-equivalent of cations will move with the current, and $\frac{a}{c+a}$ of a gram-equivalent of anions will move against the current.

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[1] *Ztschr. phys. Chem.* **4**, 140 (1889).

$\frac{c}{c+a}$ of cations have moved from a region of greater to one of less osmotic pressure. The work is:—

$$\frac{c}{c+a} RT \ln \frac{p_1}{p_2}.$$

But $\frac{a}{c+a}$ of anions have moved from a region of lower into one of higher osmotic pressure. The work done upon them is:—

$$\frac{a}{c+a} RT \ln \frac{p_1}{p_2}.$$

The total gain is the difference between these two:—

$$\frac{c-a}{c+a} RT \ln \frac{p_1}{p_2}.$$

Equating this against the electrical energy πe_0, we have —

$$\pi = \frac{c-a}{c+a} \frac{RT}{e_0} \ln \frac{p_1}{p_2};$$

or,

$$\pi = \frac{c-a}{c+a} 0.0002\ T \log \frac{p_1}{p_2}.$$

If c is greater than a the more dilute solution is positive, as already stated, and the current flows on the outside from the more dilute solution to the more concentrated. If a is greater than c, the more dilute solution is negative, and the current flows in the opposite direction.

If the velocities of the two ions are equal ($c=a$), the right member of the above equation becomes zero, and there is no electromotive force. It is, therefore, impossible to construct a liquid element from solutions of an electrolyte whose cation and anion have the same velocities. If the valence of either ion is greater than unity, this must be taken into account. If we represent the valence of the cation by v, and that of the anion by v_1, the above expression becomes —

$$\pi = \frac{\frac{c}{v} - \frac{a}{v_1}}{c+a} 0.0002\ T \log \frac{p_1}{p_2}.$$

Nernst prepared liquid elements and determined their electromotive force. He then calculated the electromotive force from the above equation, and compared the values found experimentally with those from calculation.

The following element already referred to was constructed: —

$$\mathrm{Hg}-\mathrm{HgCl}-\underset{\frac{n}{10}}{\mathrm{KCl}}\overset{1}{-}\underset{\frac{n}{100}}{\mathrm{KCl}}\overset{2}{-}\underset{\frac{n}{100}}{\mathrm{HCl}}\overset{3}{-}\underset{\frac{n}{10}}{\mathrm{HCl}}\overset{4}{-}\underset{\frac{n}{10}.}{\mathrm{KCl}}-\mathrm{HgCl}-\mathrm{Hg}.$$

The potential differences at the ends are equal and opposite, and therefore equalize one another. The four differences in potential which must be taken into account are indicated above. But the potential differences are dependent upon the relative, not upon the absolute osmotic pressures. The potentials at 2 and 4 are, therefore, equal and opposite, and can also be left out of account. This leaves the potentials at 1 and 3, and these can be calculated by the method already given. Let c_1 and a_1 be the relative velocities of potassium and chlorine ions, and c_2 and a_2 the relative velocities of hydrogen and chlorine ions; the electromotive force of this element would be calculated as follows, from the equation just deduced. The electromotive force would be the difference between these two potentials: —

$$\pi=\frac{c_1-a_1}{c_1+a_1}\frac{RT}{e_0}\ln\frac{p}{p_1}-\frac{c_2-a_2}{c_2+a_2}\frac{RT}{e_0}\ln\frac{p'}{p_1'},$$

p and p_1 are the osmotic pressures of the potassium and chlorine ions in the more concentrated and more dilute solutions, respectively; p' and p_1' the osmotic pressures of the hydrogen and chlorine ions in the solutions of hydrochloric acid: —

$$\frac{p}{p_1}=\frac{p'}{p_1'}.$$

Introducing this into the last equation, we have —

$$\pi=\left(\frac{c_1-a_1}{c_1+a_1}-\frac{c_2-a_2}{c_2+a_2}\right)\frac{RT}{e_0}\ln\frac{p}{p_1};$$

or,

$$\pi=\left(\frac{c_1-a_1}{c_1+a_1}-\frac{c_2-a_2}{c_2+a_2}\right)0.0002\ T\log\frac{p}{p_1}.$$

This is the expression for calculating the electromotive force in liquid elements like the above where the valence of the cation is the same as that of the anion. If they are different, we will represent the valence of the cations by v and v', and that of the anions by v_1 and v_1'; the equation for the electromotive force would then become —

$$\pi = \left\{ \frac{\frac{c_1}{v} - \frac{a_1}{v_1}}{c_1 + a_1} - \frac{\frac{c_2}{v'} - \frac{a_2}{v_1'}}{c_2 + a_2} \right\} 0.0002\ T \log \frac{p}{p_1}.$$

The electromotive force of the liquid elements which have been studied, as calculated from the above equation, agrees with that measured, to within the limits of experimental error.

It should be observed that the expression deduced above holds only for the potential at the contact of solutions of the same electrolyte, the solutions being of different concentrations. If different electrolytes are used, we have no general means of calculating the potential at their surface of contact.

It should be stated before leaving the subject of liquid elements, that the potential at the contact of two solutions is usually not great, and that the electromotive force of liquid elements is in general not large.

Sources of Potential in a Concentration Element. — We may now analyze more closely the electromotive force in a concentration element in the light of what we have learned about the liquid element. Thus far we have dealt with the concentration element as if the only sources of the potential were at the points of contact of the electrodes and the solutions. And indeed this is practically true in the cases of the concentration element which we have studied.

We have learned from the study of the liquid element that the plane of contact of two solutions of an electrolyte is also a seat of potential. In the concentration element there is always such a contact between two solutions of the electrolyte, and this must be a source of potential. In the concentration element which we have studied, this potential is so small that it can practically be neglected. While the potential between solutions is usually small, it may, however, easily assume proportions which must be taken into account. We must now see how it is possible to calculate the potential at the contact of the two solutions in the concentration element. We can then analyze the electromotive force of a concentration element into its three constituents, and calculate the magnitude of the potential at each electrode, and also at the surface of contact of the electrolytes.

Let the potential at one electrode be π', at the other electrode π'', and at the contact of the two electrolytes π'''. The values of these potentials are calculated by means of the following formulas:—

$$\pi' = 0.0002\ T \log \frac{P}{p_1};$$

$$\pi'' = -0.0002\ T \log \frac{P}{p_2};$$

$$\pi''' = 0.0002\ T \frac{c-a}{c+a} \log \frac{p_1}{p_2}.$$

These equations obtain for univalent ions. If the valence of the ion is greater than one, this must be taken into account in the way already described. The sum of the three potentials must then be the potential of the concentration element.

$$\pi' + \pi'' = -0.0002\ T \log \frac{p_1}{p_2};$$

$$(\pi' + \pi'') + \pi''' = 0.0002\ T \frac{2a}{c+a} \log \frac{p_2}{p_1}.$$

This must be the same as the equation already deduced (p. 391) for the concentration element. It will be seen to be the case, if we consider that $n_i = 2$, and v for univalent ions equals 1.

We can thus calculate the magnitude of the three sources of potential in a concentration element of the first class. An element of this class has been chosen, since the relations are somewhat simpler. The main sources of potential are at the contact of electrode and electrolyte, while a very small potential exists at the contact of the two electrolytes. In elements of this kind it is perfectly clear that there is no potential where the two electrodes come in contact, because these are of the same metal.

Chemical Elements.—In the elements which we have thus far considered, the electrical energy is not produced at the expense of chemical energy, as Le Blanc[1] clearly points out. Since the intrinsic or chemical energy of the substances in the cell remains unaltered, the electrical energy produced in the cell must come mainly from the heat of surrounding objects, which is converted into electrical energy in the cell.

There are, however, forms of elements in which chemical energy is converted into electrical, and these are termed *chemical elements.* Such elements may transform the chemical energy quantitatively into electrical; or only a portion of the chemical energy may be transformed into electrical, the remainder appearing as heat; or, finally, a part of the electrical energy may come from the chemical energy, and the remainder from the heat taken up by the cell and transformed into electrical energy.

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[1] *Lehrbuch der Elektrochemie*, p. 160.

There is thus no very sharp distinction between chemical elements and non-chemical elements. There are, however, elements in which most of the electrical energy comes from chemical energy, and these we will include under the head of chemical elements, to distinguish them from those elements where no chemical energy is converted into electrical.

It is obvious that there might be a large number of elements in which a small portion of the electrical energy was produced from chemical energy, and the remainder from heat energy. Such would obviously not fall into either of the above classes.

We will take as a type of the chemical element the *Daniell element*, which consists of zinc immersed in a solution of zinc sulphate, and copper immersed in a solution of copper sulphate. Zinc dissolves, passing into solution as ions, while ions of copper separate from the solution in the metallic form. The zinc electrode is therefore negative, and the copper positive; the current passing on the outside from the copper to the zinc.

In calculating the electromotive force of the Daniell element, the solution-tension of both the copper and the zinc must be taken into account. In the elements which we have thus far considered, both electrodes were of the same metal. The solution-tension of the metal was, therefore, the same upon both sides of the cell, and being of equal value and opposite sign, it disappeared from the equation for the electromotive force of the element. Whenever the electrodes are of different substances, their solution-tensions being of unequal values must be taken into account.

The application of our fundamental equation to the electromotive force of the Daniell element will serve as an example of the way in which it may be applied to other well-known elements. The electromotive force is equal to the difference in potential at the two electrodes, since the potential at the contact of the zinc sulphate and copper sulphate is so slight that we can practically disregard it.

Representing the potential at the two electrodes by π_1 and π_2, we have —

$$\pi_1 = \frac{RT}{2\,e_0} \ln \frac{P}{p};$$

$$\pi_2 = \frac{RT}{2\,e_0} \ln \frac{P_1}{p_1};$$

in which P and P_1 are the solution-tensions of the two metals: —

$$\pi_1 - \pi_2 = \pi = \frac{RT}{2\,e_0}\left(\ln\frac{P}{p} - \ln\frac{P_1}{p_1}\right).$$

In the light of this example, the application of the conceptions here developed to other special cases should be a simple matter.

Oxidation and Reduction Elements. — A type of elements which illustrates very well the transformation of chemical energy into electrical, is known as the oxidation and reduction elements. These must be considered very briefly. In a paper on "Chemical Action at a Distance,"[1] Ostwald described such phenomena as the following. If we have a solution of ferrous chloride in contact with a solution of potassium chloride which contains free chlorine, and plunge carbon or platinum electrodes into the two liquids, we have an element. It is not even necessary that the two solutions should come in contact; they may be separated by an electrolyte, say a solution of potassium chloride. Ostwald recommended the following experiment: Two beakers are filled — the one with a solution of ferrous chloride, the other with a solution of potassium chloride saturated with chlorine. Platinum electrodes are introduced into each vessel, and are connected with each other through a galvanometer. The two beakers are connected by means of a siphon filled with a solution of potassium chloride, and the ends loosely stoppered with rolls of filter-paper. When the circuit is closed the galvanometer shows that a current is passing; and it flows in the liquid from the ferrous chloride to the chlorine. Within the cell the ferrous ion passes over into the ferric ion, and at the same time an equivalent number of chlorine ions are formed on the other side of the cell. There is evidently an oxidation of the iron and a reduction of the chlorine taking place.

We must now define oxidation and reduction in an electrical sense. An *electrical oxidizing agent* is one in which there is a tendency to form new negative charges, or to cause positive charges to disappear. An *electrical reducing agent* is one in which there is a tendency to form new positive ion charges, or to cause negative charges already present to disappear.

In the above element the ferrous ion takes up a positive charge from the electrode with which it is in contact, becoming a ferric ion, and the corresponding negative charge is taken from the other electrode by the chlorine, which becomes an anion. The electrode immersed in the reducing agent ($FeCl_2$) is, therefore, the anode, while the electrode immersed in the oxidizing agent is the cathode.

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[1] *Ztschr. phys. Chem.* **9**, 549 (1894).

As Ostwald observes, this element seems to represent *chemical action as taking place at a distance,* — the chlorine in one vessel converting the ferrous iron in another vessel into ferric iron. But as we have just seen, it is readily explained in the light of the theory of electrolytic dissociation.

The measurement of the electromotive force of a number of such elements was carried out in Ostwald's laboratory by W. D. Bancroft.[1] The more important conclusions at which he arrived are: —

The electromotive force is an additive property, *i.e.* the sum of two constants, one depending on the oxidizing agent, the other on the reducing agent.

It is independent of the concentration, and of the nature of the electrodes, if these are not attacked by the electrolytes.

It is also independent of the nature of the electrolyte used in the siphon.

The Gas-battery. — The typical gas-battery consists of an electrolyte, two gases which can act chemically upon one another, and two platinum electrodes which are partly surrounded by the electrolyte, and partly by the gases.

Take as a simple example, hydrogen over one electrode and chlorine over the other, the electrolyte hydrochloric acid, and the electrodes platinum. Hydrogen and chlorine will pass into solution at the two poles until there is an equilibrium between the force driving these substances into solution (solution-tension), and the osmotic pressure of the hydrochloric acid solution, which acts against the above-named force. The hydrogen pole is negative, since the solution-tension of the hydrogen is greater than the osmotic pressure of the solution; the hydrogen atoms becoming ions by taking positive electricity from the platinum electrode, which thus becomes negative. Exactly the opposite result is obtained at the other electrode, chlorine atoms becoming ions by taking negative electricity from the electrode, which therefore becomes positive.

Ostwald[2] has shown that the theory of Nernst can be applied also to the electromotive force of the gas-battery. He has worked out even a simpler case than the one given above. We will take up first the simplest possible case, where we have the same gas, say hydrogen, over both electrodes, the hydrogen upon the two sides being at different pressures.

The action of such an arrangement would be, as Ostwald shows, to equalize the pressure of the gas on the two sides of the cell. Hydrogen must pass into solution as ions upon the side where it is under the greater pressure, and ions of hydrogen must separate as gas upon the other side of the cell. Upon the side where hydrogen atoms are becoming ions, they take positive electricity from the electrode, which becomes negative, and the other electrode positive, because positive hydrogen ions are giving their charges up to it. We have here an analogue of the concentration element, and the electromotive force can be calculated in a similar manner.

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[1] *Ztschr. phys. Chem.* **10**, 387 (1892).

[2] *Lehrb. d. Allg. Chem.* II, p. 895.

The electromotive force of this element also is the difference in the potential upon the two sides: —

$$\pi = \frac{RT}{ve_0} \ln \frac{P}{p_2} - \frac{RT}{ve_0} \ln \frac{P}{p_1},$$

where P is the solution-tension of hydrogen, and p_1 and p_2 the pressures of the hydrogen gas upon the two sides. The solution-tension, being the same upon both sides of the cell, disappears as in the concentration element, and then we have —

$$\pi = \frac{0.0002\ T}{v} \log \frac{p_1}{p_2}.$$

Since for the hydrogen molecule, $v = 2$, we have —

$$\pi = 0.0290 \log \frac{p_1}{p_2}.$$

Ostwald[1] has also calculated the electromotive force for a gas-battery consisting of two gases. But as this has been worked out much more fully by Smale,[2] we will turn to his work.

Take the case of oxygen at one pole and hydrogen at the other.

Let P_1 be the solution-tension of hydrogen.

Let P_2 be the solution-tension of oxygen.

Let T be the absolute temperature.

The potential at the hydrogen pole is —

$$\pi_1 = 0.0002\ T \log \frac{P_1}{p_1}.$$

Since the solution-tension of oxygen is negative, —

$$\pi_2 = 0.0002\ T \log \frac{p_2}{P_2};$$

$$\pi_1 - \pi_2 = \pi = 0.0002\ T \log \frac{P_1}{p_1} - 0.0002\ T \log \frac{p_2}{P_2};$$

$$\pi = 0.0002\ T \log \frac{P_1}{p_1} + 0.0002\ T \log \frac{P_2}{p_2}.$$

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[1] *Loc. cit.*

[2] *Ztschr. phys. Chem.* **14**, 577, and **16**, 562.

The theoretical consequences of this equation are very interesting. P_1 and P_2, the solution-tensions of the gases, *are independent of the nature and concentration of the electrolyte used on the two sides of the element;* and p_1 and p_2 are practically constant for solutions of nearly the same dissociation.

Smale[1] has tested this point, using seven acids, three bases, and seven salts. The concentrations for the same electrolyte vary in most cases from 0.1 to 0.001 normal. He found that the electromotive force of the hydrogen-oxygen battery was practically constant, independent of both the nature and concentration of the electrolytes used beneath the gases.

A few results taken from the work of Smale will bring out this fact.

Electrolyte Used	Concentration Normal	E.M.F.
HCl	0.1	0.998
HCl	0.01	1.036
HCl	0.001	1.055
KOH	0.1	1.098
KOH	0.01	1.095
KOH	0.001	1.093
K_2SO_4	0.1	1.074
K_2SO_4	0.01	1.069
K_2SO_4	0.001	1.069

The results thus agree satisfactorily with the deduction from theory.

If instead of oxygen other gases, as chlorine, are used, the electromotive force depends upon the concentration of the electrolyte, which also agrees with theory, as is shown by Smale.

This work of Smale furnishes then another beautiful experimental confirmation of the consequences of that theory, which has enabled us to calculate the electromotive force of concentration elements, liquid elements, etc.

A number of other types of elements might be taken up, and their electromotive force calculated from the method of Nernst, which, as we have already seen, is based upon Van't Hoff's laws of osmotic pressure and Arrhenius' theory of electrolytic dissociation. This is, however, not necessary, since the application to special cases is simple if the fundamental principles are once grasped.

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[1] *Loc. cit.*

MEASUREMENT OF DIFFERENCES OF POTENTIAL BETWEEN METALS AND ELECTROLYTES — CALCULATION OF THE SOLUTION-TENSION OF METALS

Differences of Potential between Metals and Electrolytes. — It is obvious from our studies of the action of the primary cell, that when a metal is immersed in a solution of one of its salts, there is established a difference in potential between the metal and the solution. Indeed, we have seen that this is the chief source of the electromotive force in such elements. The cause of this difference in potential we have learned is, on the one hand, the solution-tension of the metal tending to drive ions from the metal into the solution, and the osmotic pressure of the solution acting counter to this, tending to cause the cations already present to separate on the electrode in the metallic condition. The result is the formation of the Helmholtz double layer, and a difference in potential between the metal and the solution. It is very desirable to know the magnitude of these potential differences, and to the measurement of such differences we shall now turn.

Measurement of Individual Differences of Potential. — A number of methods have been devised and used for measuring differences of potential between metals and solutions. Reference only can be made to that involving the use of drop-electrodes.[1] We shall now study in some detail the method involving the use of the "normal electrode." This method is based upon the use of an electrode whose potential is known. This is connected with the electrode whose difference in potential it is desired to measure, and the electromotive force of the whole determined. Since the potential of the normal electrode is known, that of the electrode in question is determined at once, the electromotive force of the two when combined being the difference between the potentials on the two sides.

The form of "normal electrode" used by Ostwald is shown in Fig. 52. The bottom of a glass tube *A*, about 8 cm. high, and 2 to 2½ cm. in diameter, is covered with mercury. Over the mercury is placed a layer of mercurous chloride, and the glass vessel is then filled with a normal solution of potassium chloride. A platinum wire, *Pt*, passed into a glass tube and protruding beyond its end, dips into the mercury. This serves as one electrode. The other glass tube, *t*, passing through the cork, is filled also with the normal solution of potassium chloride. The glass tube, t_1, at the end of the rubber tube, is inserted into the liquid whose potential against a given metal it is desired to measure. The metal serves as the second electrode. The electromotive force of the whole system is now measured. Knowing the potential on the one side, that on the other is obtained at once.

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[1] Ostwald: *Ztschr. phys. Chem.* **1**, 583 (1887); see also ***Outlines of Electrochemistry***, Jones (Elec. Rev. Pub. Co.).

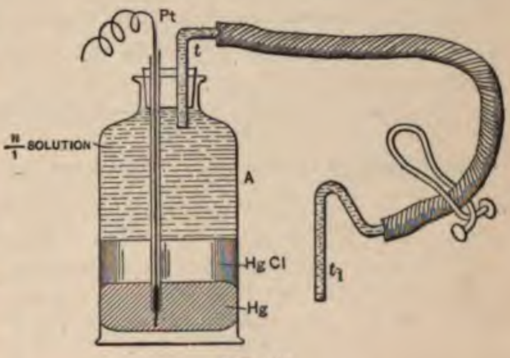

Fig. 52.

If the liquid in the electrode whose potential it is desired to measure acts chemically upon potassium chloride, a solution of some indifferent substance is interposed between the two. Thus, if we were measuring the difference in potential between lead and lead nitrate, a solution of some neutral nitrate (as potassium or sodium) would be interposed in the circuit. The use of potassium chloride is very desirable, since the potassium and chlorine ions move with very nearly the same velocity, and, therefore, any potential difference at the contact of the two electrolytes would be very small.

The potential of the normal electrode just described is 0.56 volt. The metal is positive, the electrolyte negative, which means that there is a tendency for the mercury ions present to separate from the solution as metallic mercury; and this tendency is expressed in potential by 0.56 volt.

In such measurements the potential of the metal is taken as zero, and the electrolyte expressed as either positive or negative. The normal electrode just described has then a potential of -0.56 volt.

By means of this normal electrode, potential differences between metals and electrolytes can be easily measured.

Let us take as an example, the potential difference of magnesium against a normal solution of magnesium chloride. The "normal electrode" is connected with a vessel containing a normal solution of magnesium chloride, into which a bar of magnesium dips. The electromotive force of this combination was measured and found to be 1.791 volts. We know that the electromotive force, π, of this element is expressed thus:—

$$\pi = \frac{RT}{2\,e_0}\ln\frac{P}{p} - \frac{RT}{e_0}\ln\frac{P_1}{p_1}, \tag{1}$$

in which P is the solution-tension of magnesium, p the osmotic pressure of the magnesium ions in the solution, 2 the valence of magnesium; P_1 the solution-tension of mercury, and p_1 the osmotic pressure of the mercury ions in the solution. We have just seen, however, that,

$$\frac{RT}{e_0}\ln\frac{P_1}{p_1} = -0.56 \text{ volt.}$$

Substituting in equation (1) we have—

$$1.791 = \frac{RT}{2\,e_0}\ln\frac{P}{p} + 0.56,$$

or,

$$\frac{RT}{2\,e_0}\ln\frac{P}{p} = 1.231 \text{ volts.}$$

But,

$$\frac{RT}{2\,e_0}\ln\frac{P}{p} = 0.029\log\frac{P}{p};$$

therefore,

$$0.029\log\frac{P}{p} = 1.231 \text{ volts.}$$

The difference in potential between magnesium and a normal solution of magnesium chloride is, then, 1.231 volts.

The differences of potential between a number of metals and normal or saturated solutions of their salts have been measured by Neumann, working in Ostwald's laboratory. The following data are taken from the results which he obtained:—

Metal	Sulphate	Chloride
	Volts	Volts
Magnesium	+ 1.239	+ 1.231
Aluminium	+ 1.040	+ 1.015
Zinc	+ 0.524	+ 0.503
Cadmium	+ 0.162	+ 0.174
Iron	+ 0.093	+ 0.087
Cobalt	− 0.019	− 0.015
Nickel	− 0.022	− 0.020
Tin	——	− 0.085
Lead	——	− 0.095
Copper	− 0.515	——
Mercury	− 0.980	——
Silver	− 0.974	——
Gold	——	− 1.356
Platinum	——	− 1.066

Effect of the Nature of the Anion. — The question as to the effect of the anion on the potential between the metal and the solution was raised by Neumann. In addition to sulphates and chlorides, which gave very nearly the same results, he used also nitrates and acetates. The results in the latter cases were very different from those obtained with the chlorides and sulphates. The discrepancies in the case of the acetates may be accounted for in part as due to differences in the degree of dissociation of the different salts. In the case of the nitrates the NO_3 ion undoubtedly has some action on the metal electrodes. If, however, we take all of these possibilities into account, there are still discrepancies which are not satisfactorily explained.

To test the effect of the anion on the potential difference, Neumann[1] prepared twenty-three salts of thallium, and studied the potential between the metal and their solutions at different concentrations. These include the thallium salts of seventeen organic acids, five inorganic acids, and the hydroxide. A few of his results are given below.

SALTS OF THALLIUM	$\frac{n}{10}$	$\frac{n}{50}$	$\frac{n}{100}$
	Potential	Potential	Potential
Hydroxide	0.670	0.704	0.715
Nitrate	0.671	0.7055	0.716
Formate	0.675	0.7045	0.715
Acetate	0.677	0.7055	0.715
Malonate	0.678	0.705	0.715
Tartrate	0.677	0.705	0.715
Benzoate	0.680	0.705	0.7155

These results show that for equally dissociated substances, the anion is without influence as far as the salts of thallium are concerned.

Calculation of the Solution-tension of Metals. — The difference in potential between a metal and the solution of the electrolyte in which it is immersed is due, as we have seen, to the solution-tension of the metal, and to the osmotic pressure of the cations in the solution. If we know the value of this potential difference and of the osmotic pressure of the cations in the solution, it is obvious that we can calculate the solution-tension of the metal. We have seen that the potential difference, which we will call π, is expressed thus: —

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[1] *Ztschr. phys. Chem.* **14**, 225 (1894).

$$\pi = \frac{0.058}{n_e} \log \frac{P}{p},$$

where n_e is the valence of the cation, p the osmotic pressure of the cations in the solution, and P the solution-tension of the metal. If π and p are known, P can be calculated at once. Thus: —

$$\log P = \frac{\pi n_e}{0.058} + \log p.$$

The solution-tensions of some of the more common metals calculated from this equation, using the values of π as found by Neumann, are given in the following table. The values of π for the chlorides are used whenever they were determined; when this is not available, the value for the sulphate was used. The value of the osmotic pressure of the cations in the normal solutions is taken as 22 atmospheres.

	ATMOSPHERES
Magnesium	10^{44}
Zinc	10^{18}
Aluminium	10^{13}
Cadmium	3×10^{6}
Iron	10^{4}
Cobalt	2×10^{0}
Nickel	1×10^{0}
Lead	10^{-3}
Mercury	10^{-16}
Silver	10^{-17}
Copper	10^{-20}

The Tension Series. — When the metals are arranged as above in the order of their solution-tensions, we have what is known as the tension series. The position of a metal in the tension series, like its position in the Periodic System, conditions many of its properties. Thus, a metal anywhere in the series will tend to precipitate from its salts any metal lower in the series. Thus, it is well known that zinc will precipitate copper from its salts, and so on.

A metal at any point in the series, when made one pole of a battery against a metal lower in the series as the other pole, will throw off ions into solution, and thus become the negative pole. Thus, zinc is the negative pole in almost all elements in which it occurs. The position of an element in the tension series is thus a matter of fundamental importance, being very closely connected with the inherent nature of the metal itself.

Constancy of Solution-tension. — It was supposed for a time that the solution-tension of a metal is a characteristic constant for the substance. This view was held by Ostwald and developed in his *Lehrbuch*. On page 852 it is stated that "the value P, of the electrolytic solution-pressure, is a constant peculiar to the metal, which depends upon the temperature only, and generally increases with increasing temperature."

So far as we know this holds for a given solvent, but does not apply to different solvents. Jones[1] has found that the solution-tension of metallic silver, when immersed in an alcoholic solution of silver nitrate, is only about one-twentieth of that in an aqueous solution. We can, therefore, regard solution-tension as a constant only for any given solvent in which the salts of the metal are dissolved. Indeed, this is what we would expect, when we consider that nearly every substance dissolves differently in, or has a specific solution-tension toward, every solvent. If the substances which dissolve readily in solvents vary so greatly from solvent to solvent, as we know they do, why should not substances which are only slightly soluble, such as the metals, show this same difference?

Kahlenberg[2] has extended the work which was begun by Jones, using a number of metals and quite a number of solvents. He confirms the above conclusion that the solution-tensions of metals vary greatly from solvent to solvent. Quite recently, Jones and Smith[3] have shown that the solution-tension of zinc in water is 10^8 times its solution-tension in ethyl alcohol.

Difference in Solution-tensions of Metals. Chemical Action at a Distance. — Reference[4] has already been made to the paper by Ostwald on "Chemical Action at a Distance." Under that same head he describes an experiment which must be referred to here. Ostwald begins his paper by calling attention to the fact that amalgamated zinc is not dissolved by dilute acids, but if the zinc is surrounded by a platinum wire, it is dissolved by the acid. It is not even necessary for the platinum wire to surround the zinc, for if the wire touches the zinc at any one point, solution will take place.

Ostwald suggests that the zinc and platinum wire be joined at one place, and then the free ends of both immersed in a vessel containing, say, potassium sulphate. Let a screen of some porous material be placed between these free ends of the platinum and zinc, so that the salt solution around the one is separated from that around the other. He then asks the question, to which metal must sulphuric acid be added in order that the zinc may be dissolved by the acid?

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[1] *Ztschr. phys. Chem.* **14**, 346 (1894). *Phys. Rev.* **2**, 81 (1894).

[2] *Journ. Phys. Chem.* **3**, 379 (1889).

[3] *Amer. Chem. Journ.* **23**, 397 (1900).

[4] *Ztschr. phys. Chem.* **9**, 540 (1892).

"The question seems at first sight to be absurd; since in order that the zinc should dissolve, it appears to be self-evident that the acid should be added to the zinc. If we carry out the experiment, we find exactly the reverse to be true. The zinc does not dissolve rapidly, if acid is added to the solution of potassium sulphate around the zinc. If, on the contrary, the acid is added to the solution around the platinum, the zinc dissolves with a copious evolution of hydrogen gas. The hydrogen appears on the platinum, as is always the case when zinc is in combination with platinum. To dissolve the zinc under the conditions described, the solvents must not be allowed to act on the metal to be dissolved, but on the platinum which is in contact with the zinc."

A number of other cases are cited.

Zinc in sodium chloride behaves in the same manner when hydrochloric acid is added to the platinum. Cadmium also behaves like zinc. Tin, surrounded by sodium chloride, dissolves when hydrochloric acid is added to the platinum. Aluminium behaves like tin. Silver connected with platinum dissolves in sulphuric acid when a few drops of chromic acid are added to the platinum. Gold dissolves in sodium chloride, if chlorine is brought in contact with the platinum.

Experiment to demonstrate Chemical Action at a Distance. — Fill a beaker with a solution of potassium sulphate. Take a piece of glass tubing about 10 cm. long and 2 cm. wide, and close the lower end with vegetable parchment. Fit a bar of pure zinc, about 10 cm. long, tightly into a cork which just closes the top of this glass tube. Fill the glass tube with some of the same solution of potassium sulphate, and insert the bar of zinc — the cork closing the top of the glass tube. Around the top of the zinc bar above the cork wrap a piece of platinum wire of sufficient length to reach nearly to the bottom of the beaker, when the glass tube is introduced into the beaker in the manner to be described hereafter. The free end of the platinum wire should be coiled upon itself a number of times, or it is better if it is connected with a piece of platinum foil a few centimetres square, so as to expose a larger surface.

The glass tube is now immersed in the beaker until the surface of the solution in the tube is only a centimetre or two above the surface of the solution in the beaker, the free end of the platinum wire, or the platinum foil, being allowed to rest on the bottom of the beaker.

If a few drops of sulphuric acid are introduced into the potassium sulphate just around the bar of zinc, the zinc will be very slightly affected. But if a few drops of sulphuric acid are poured upon the coiled end of the platinum wire, or upon the platinum foil, the zinc will dissolve rapidly in the neutral potassium sulphate which surrounds it, and a copious evolution of hydrogen will take place from the platinum, where it is in contact with the sulphuric acid. After a few moments the presence of zinc can be demonstrated in the inner tube, by any of the well-known reactions for zinc.

As Ostwald states, similar phenomena have long been known. More than forty years ago Thomsen[1] described a galvanic element, which consists of copper in dilute sulphuric acid, and carbon in a chromate mixture. When the carbon and copper were connected, the metal dissolved as the sulphate in sulphuric acid, in which copper alone is not soluble. Becquerel,[2] observed a similar phenomenon in the case of the element $Cu{-}ZnSO_4{-}ZnSO_4{-}Zn$. While many similar facts were known, there was no rational explanation offered to account for them until Arrhenius proposed the *Theory of Free Ions.*

It is almost self-evident that the phenomenon is closely connected with electrical changes. Ostwald demonstrated this by introducing between the metal and the platinum a fairly sensitive galvanoscope. When the acid was added to the platinum, the presence of a current was shown by the throw of the instrument.

The explanation of this phenomenon is perfectly simple, now that we have the theory of electrolytic dissociation and are familiar with its application to the primary cell.

When metallic zinc is immersed in a solution of a neutral salt, like potassium sulphate, it sends, in consequence of its own solution-tension, a certain number of zinc ions into the solution. The zinc is thus made negative, and the solution, which has received the positive ions, positive. This continues until a definite difference in potential between metal and solution is established. The amount of metal required to effect this condition is, as we have seen, so small that it cannot be detected by any chemical means.

The zinc cannot dissolve further, because of the excess of positive ions in the solution. In order that more zinc may pass into solution, some of these positive ions must be removed. If the zinc is in combination with another metal, such as platinum, the latter takes the same negative charge as the zinc. When the platinum is immersed in the solution, it attracts the excess of positive ions in the solution, and these collect upon the platinum.

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[1] *Pogg. Ann.* **111**, 192 (1860).

[2] *Ann. Chim. Phys.* [2], **41**, 5 (1829).

We would expect the excess of positive ions in the solution to give up their charge to the negative platinum, and separate from the solution, or, in case of potassium decompose the water which is present. This depends both upon the nature of the ion and of the electrode. If the positive ion is the potassium of potassium sulphate, the difference in potential produced by introducing the zinc is not sufficient to cause this ion to lose its charge to the platinum. If sulphuric acid is added to the platinum, the difference in potential produced by introducing the bar of zinc, is sufficient to compel the hydrogen to give up its positive charge to the platinum, and separate as ordinary hydrogen. The platinum, having received positive electricity from the hydrogen ions, conducts this over to the zinc. The zinc becomes less negative than before the hydrogen separated at the platinum, and the difference in potential between the zinc and the surrounding solution is less than before. More zinc dissolves or passes over into ions, more hydrogen ions give up their charge to the platinum and separate as gas; and this continues until all of the zinc has dissolved, or all of the hydrogen ions have separated as gas.

As Ostwald observes, this explanation shows not only why the acid must be added to the platinum and not to the zinc, but throws light also on the problem of the solution of metals in general. A word or two on this subject. It has long been known that pure zinc does not dissolve in acids, while impure zinc readily dissolves. It is quite evident that the zinc in the two cases has the same tendency to dissolve. Pure zinc dissolves readily when in contact with a metal, such as platinum, which has a small solution-tension. As we have seen from the foregoing explanation, the difference is not in the solution of the zinc, but in the ease with which the hydrogen can escape from the solution. The presence of a metal with small solution-tension allows this to take place more readily, and this is the reason that impure zinc dissolves in acids.

The reason why pure zinc does not dissolve in acids is because this metal has a strong positive solution-tension; it sends positively charged ions into solution under a high solution-tension, and, therefore, opposes the separation of any other positive ion, like hydrogen, upon it. Pure zinc, therefore, does not dissolve in acids, because the hydrogen ions cannot give up their positive charges and escape.

When a metal like platinum, which has a small solution-tension, is present, the hydrogen can easily give up its charge to this metal and escape as gas. The zinc, because of its high solution-tension, and because the hydrogen cations can so easily escape, then dissolves.

To repeat the essential steps in the explanation of the experiment described above: Pure zinc immersed in potassium (or any soluble) sulphate, to which sulphuric acid is added, or in a solution of pure sulphuric acid itself, does not dissolve because the zinc has such a high solution-tension that the hydrogen ions cannot give up their charge to it and escape. The zinc, however, throws a few ions into solution and becomes negatively charged. If now the zinc is connected with platinum, which has a small solution-tension, and the acid added to the platinum, the hydrogen ions can easily give up their charge to the platinum and escape as gas. The platinum, which was at the potential of the zinc with which it is in combination, now becomes positive with respect to the zinc, and a positive charge therefore flows from the platinum to the zinc. The zinc, having received positive electricity, can begin dissolving anew, and continue to pass into solution as long as it receives positive electricity from the platinum — as long, therefore, as there are any hydrogen ions in the solution to furnish positive electricity to the platinum. Or, as we are accustomed to express it, as long as there is any acid in contact with the platinum.

This subject will be concluded with a paragraph from this fascinating paper by Ostwald: "We see that the usual explanation, that solution takes place *because* of galvanic currents between the zinc and the other metals, is not in strict accord with the facts. The galvanic currents are inseparably connected with the process of solution, but they are not the primary causes of the solution. They are set up, rather, by the process of solution, which they must necessarily accompany since solution is a question of ion formation and disappearance. If it is possible for the positive ions present to separate in any way from the solvent, solution takes place."

ELECTROLYSIS AND POLARIZATION

Passage of Electricity through Electrolytes. — When the two electrodes of a battery, or of any other source of electricity, are placed in a solution of an electrolyte, the current flows through the solution from one electrode to the other. Much confusion has existed in the naming of these electrodes. If we refer to them as positive and negative, this is ambiguous. If we name them in terms of the direction of the flow of current, we must specify whether we mean the flow on the outside or on the inside of the cell. The best method is to call that electrode the cathode toward which the current flows in the cell, and the other electrode the anode.

The current can pass through solutions of electrolytes, as we have seen, in only one manner; *i.e.* by a simultaneous movement of the ions in the solution — the cations carrying the positive charge toward the cathode, the anions the negative charge toward the anode. These ions give up their charges to the respective electrodes or poles, and thus become atoms or groups of atoms. These may then separate from the solution, or secondary reactions may take place. This process is known as *electrolysis.*

The actual process at the poles may be quite different, in many cases, from what was for a long time supposed; but this will be considered a little later.

Products of Electrolysis. — When the ions give up their charges to the electrodes, they may be capable of an independent existence, or they may not, depending upon their nature. Many cations, such as some of the metals, are capable of such an existence, while very few anions can exist as such, after they give up their negative charge. In the latter case they may decompose into entirely new products, or may react with some other substance present and give rise to secondary products. We must distinguish, then, between *primary* and *secondary* products of electrolysis.

The primary products of electrolysis are the metals, which separate as such from the solutions of their salts; also other elements which separate as such, *e.g.* hydrogen, chlorine, etc. The attempt which has been made to place these substances among the secondary products, because the atoms polymerize to form molecules, and thus separating them from the metals which are primary products, does not seem to be well founded. It is, of course, true that two hydrogen atoms, two chlorine atoms, etc., unite to form a molecule, but does any one suppose that the molecule of a metal in the solid state is identical with the atom? The fact that the molecule of many metals is identical with the atom when the metal is dissolved in mercury, which we have seen to be true, is no argument that such is the case in the pure metal. The metallic atoms probably polymerize as much or more than the chlorine atoms.

The secondary products of electrolysis may be formed in at least four ways: —

(1) The ions may react with the water present as solvent.
(2) They may react with more of the electrolyte.
(3) They may react with the electrodes.
(4) They may decompose into entirely new products.

Polarization. — If a current is passed through an element containing metal electrodes surrounded by salts of the same metal, the electrodes are not changed, and the solutions around the electrodes are not changed essentially, although they do undergo slight changes in concentration. The difference in potential between the electrode and the surrounding solution remains, therefore, practically constant, and such electrodes are termed *non-polarizable.*

If, on the other hand, either the electrode or the electrolyte is changed appreciably by the passage of the current, the difference in potential between the two does not remain constant, but changes with the passage of the current. Such electrodes are termed *polarizable.* When such a change is effected, it always takes place in the sense to oppose the passage of the current. If two polarizable electrodes, through which a current has been passing for a time, are closed in circuit, a current will set up in the direction opposite to that which effected the polarization. This is known as the polarization current, and its electromotive force the electromotive force of polarization. A quantitative study of polarization currents will show that they gradually grow weaker and weaker.

Method of Measuring Polarization. — When a current passes through an electrolyte there is electrolysis, and consequently polarization at both poles. The electromotive force of polarization is, therefore, made up of two differences in potential between metals and electrolytes. In measuring polarization we must measure the potential at each electrode. A method has been devised for this purpose by Fuchs.[1] The following modification of this method was used by Le Blanc.[2]

The electrolyte whose polarization it is desired to study is introduced into the tube T (Fig. 53). Two electrodes connected with the element E, which furnishes the polarizing current, are introduced as shown in the figure. To measure the potential at either electrode, we connect this electrode with a normal electrode. To measure the potential at b, the arm of the normal electrode n is connected with the electrolyte in c, and the wire from the normal electrode connected with b through the arrangement for measuring electromotive force. The electromotive force of this element is then measured. Knowing the potential of the normal electrode and the potential at the contact of the two electrolytes in *c*, we know the potential at the electrode *b*. The potential at the electrode *a* can be measured in a similar manner.

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[1] *Pogg. Ann.* **156**, 156 (1875).

[2] *Ztschr. phys. Chem.* **8**, 299 (1891) ; **12**, 322 (1893) ; **13**, 163 (1894).

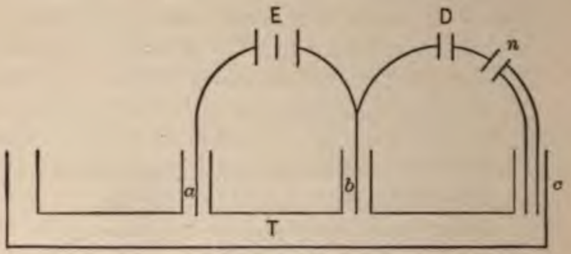

FIG. 53.

Results of the Measurement of Polarization. — If the polarizing current is at first very weak and gradually increases in strength, the current of polarization will also increase rapidly in strength. After the electromotive force of the polarizing current has become quite large, the electromotive force of the current of polarization will increase as the former increases, but more and more slowly. There is, therefore, *no maximum* of polarization attainable. It is difficult to say how high an electromotive force of polarization can be realized. Streintz[1] has described an anode polarization of seventeen volts.

Le Blanc[2] has measured the electromotive force which is required in order that a continuous steady current may be passed through an electrolyte so as to effect a continuous decomposition. He found that for a given substance under given conditions this had a definite value. This he termed the *Decomposition Value* of the substance.

If the electromotive force of the current used is smaller than the "decomposition value" of the substance in question, a throw of the galvanometer will manifest itself; but the instrument will soon return to its original position, showing that there is only an instantaneous passage of the current through the electrolyte. The "decomposition values" of electrolytes have been shown to be very interesting as throwing light on the nature of electrolysis itself. The "values" for normal solutions of a few acids, bases, and salts, taken from the paper by Le Blanc,[3] will, therefore, be given.

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[1] *Wied. Ann.* **32**, 116 (1887).

[2] *Ztschr. phys. Chem.* **8**, 299 (1891).

[3] *Ibid.*, p. 315 (1891).

ACIDS

Sulphuric acid = 1.67 volts
Nitric acid = 1.69 volts
Phosphoric acid = 1.70 volts
Monochloracetic acid = 1.72 volts
Dichloracetic acid = 1.66 volts
Malonic acid = 1.69 volts
Hydrochloric acid = 1.31 volts
Triazoic acid = 1.29 volts
Oxalic acid = 0.95 volts

BASES

Sodium hydroxide = 1.69 volts
Potassium hydroxide = 1.67 volts
Ammonium hydroxide = 1.74 volts

SALTS

Barium nitrate = 2.25 volts
Strontium nitrate = 2.28 volts
Calcium nitrate = 2.11 volts
Potassium nitrate = 2.17 volts
Sodium nitrate = 2.15 volts
Barium chloride = 1.99 volts
Strontium chloride = 2.01 volts
Calcium chloride = 1.89 volts
Potassium chloride = 1.96 volts
Sodium chloride = 1.98 volts

If we examine the results for the acids and bases, we see that the "decomposition values" do not exceed 1.75 volts, and that these values for many substances are about 1.7 volts. In the case of salts of metals which decompose water, the "decomposition values" are practically constant for the salts of a given acid, as the nitrates, chlorides, etc. The explanation of these results has been furnished by Le Blanc.

Primary Decomposition of Water in Electrolysis. — When solutions of salts, acids, and bases are electrolyzed, we obtain hydrogen or a metal at the cathode, and oxygen at the anode. If the metal of the salt is capable of decomposing water, we obtain hydrogen at the cathode; if it is not, the metal itself will separate at the cathode. How are these facts to be explained? The explanation which has been accepted for a long time is as follows: Take the case of potassium sulphate; it dissociates into the cation potassium and the anion $\overset{=}{\mathrm{SO}}_4$. The potassium moves over to the cathode and gives up its charge to this electrode. The metallic potassium acts upon water, forming potassium hydroxide, and liberates hydrogen. The $\overset{=}{\mathrm{SO}}_4$ anion moves over to the anode and gives up its charge, but it cannot escape from the solution. It acts upon water, forming sulphuric acid, and liberates oxygen at this electrode. The decomposition of the water is then not a primary result of electrolysis, but a secondary act.

This view of electrolysis has now been fundamentally changed, especially by the work of Le Blanc on the "decomposition values" of electrolytes. The view which is supported by these facts is that the decomposition of water is a *primary act of electrolysis.* Water is dissociated very slightly into hydrogen ions and hydroxyl ions, as is shown by many experiments, but especially by the small conductivity of the purest water. When a solution of potassium sulphate is electrolyzed, the potassium cations carrying the positive charge move over to the cathode. They do not give up their positive charge to the electrode; but the hydrogen ions of the water already present give up their charge to the electrode and separate as gaseous hydrogen. This leaves in the solution an equal number of hydroxyl anions, which with the potassium cations form potassium hydroxide. Similarly, the $\overset{=}{\mathrm{SO}}_4$ anions move over to the anode, but they do not give up their charge to this electrode. The hydroxyl anions of the water give up their negative charges, form water and oxygen, and leave behind an equal number of hydrogen cations, which, with the $\overset{=}{\mathrm{SO}}_4$ anions, form sulphuric acid. This explanation of the phenomena fits the facts as well as the older theory. Why should we reject the older and accept the newer view?

Evidence for the Primary Decomposition of Water in Electrolysis. — We shall not attempt to take up all the evidence[1] bearing upon this theory, but a few fundamental facts will be considered.

If in terms of the old theory the cation — say potassium — moves over to the cathode and gives up its charge, and the metal then acts upon water forming potassium hydroxide and hydrogen gas, the atomic potassium must take the positive charge from the hydrogen ion. If the potassium is able to take the charge from the hydrogen ion, it must have a greater power of holding the charge than hydrogen has. As this is the case, why should potassium ions give up their charge to the cathode when there are hydrogen ions present which hold their charge less firmly than potassium?

The objection might be raised in this connection that water is only slightly dissociated and there are, therefore, only a few hydrogen ions present. These would soon be used up and then the potassium ions would have to give up their charges in terms of the old theory. This objection has of course no foundation in fact, since the water present will continue to dissociate as fast as the hydrogen ions are used up. We know from the law of mass action that the condition which will always obtain is, that the product of the number of hydrogen ions and the number of hydroxyl ions present will be a constant.

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[1] See Arrhenius: *Ztschr. phys. Chem.* **11**, 805 (1893). Le Blanc: *Ibid.* **12**, 333 (1893). Also *Outlines of Electrochemistry*, Jones (Elec. Rev. Pub. Co.).

The evidence for the new theory furnished by the "decomposition values" of electrolytes must be considered. In terms of this theory, the electrolysis of the *salt* of any metal which decomposes water is the same as the electrolysis of the salt of any other metal which decomposes water, since in all such cases the hydrogen and oxygen which separate are the primary products of electrolysis. If this is true, then the decomposition values or electromotive force required to affect continuous electrolysis must be the same for the salt of any acid with different metals which decompose water. That such is the case is seen from the table on page 419.

Again, take the acids and bases. *Acids* dissociate into hydrogen cations and anions which depend upon the nature of the acid; and bases dissociate into hydroxyl anions and cations which depend upon the nature of the base. Take as an example sulphuric acid. In terms of the new theory of electrolysis the hydrogen cations move to the cathode, give up their charge and separate. The anion $\overset{=}{\mathrm{SO}}_4$ moves to the anode, the hydroxyl ions from the water give up their charge, form water and oxygen which escapes; an equal number of hydrogen ions from the water remaining in the solution and forming sulphuric acid with the $\overset{=}{\mathrm{SO}}_4$ anion. There must, therefore, be a maximum decomposition value for acids, which corresponds to the potential required to discharge hydrogen ions on the one hand, and hydroxyl ions on the other under these conditions. This is seen to be about 1.75 volts. If the acid yields an anion whose discharging value is lower than that of hydroxyl, its decomposition value will be less than the maximum 1.75 volts, and such is the case with the halogen acids and the organic acids. *Bases* dissociate into hydroxyl which moves to the anode and gives up its charge, and a cation which moves to the cathode. The latter does not discharge its positive charge, since it loses its charge with greater difficulty than the hydrogen cations from the dissociated water already present around this electrode. The hydrogen ions lose their charge at this pole. The electrolysis of a base is therefore the same as that of an acid like sulphuric; hydrogen ions discharged at the cathode, hydroxyl at the anode. The decomposition value of a base must therefore be the same as that of an acid like sulphuric or nitric. It must be the same as the maximum decomposition value of the acid, and such is seen at once from page 419 to be the case.

One further point to make the reasoning from decomposition values complete. Acids and bases of the same ionic concentration must have the same decomposition values, as we have just seen, since the product of the number of hydrogen and hydroxyl ions in the solutions must, from the law of mass action, be a constant. It is, however, quite different with a salt. At the cathode hydrogen is liberated and a base is formed, which means an increase in the number of hydroxyl ions around the cathode, and, similarly, the formation of an acid around the anode increases the number of hydrogen ions around this pole. Since the product of the number of hydroxyl and hydrogen ions is a constant, an increase in the number of hydroxyl ions around the cathode means a decrease in the number of hydrogen ions around this pole. And for the same reason an increase in the number of hydrogen ions around the anode would diminish the number of hydroxyl ions around this pole. Both of these influences would tend to increase the decomposition value of the compound.

Here again fact and theory are in perfect accord. A comparison of the decomposition values of acids and bases with those of salts will show that the latter are considerably larger than the maximum values for the former.

The evidence for the primary decomposition of water in electrolysis is then complete as far as the decomposition values for acids, bases, and salts are concerned.

The Discharging Potential of Ions. Electrolytic Separation of the Metals. — When a current is passed through a solution of several electrolytes, all of the ions present take part in conducting the current. The amount of current which will be carried by any kind of ions will depend upon their relative numbers and their relative velocities. When the different kinds of cations reach the cathode, or anions the anode, it is not necessary that all kinds should separate. It requires a certain difference in potential between the electrode and the electrolyte to cause any given ion to give up its charge to the electrode. If the difference in potential is below the discharging value for any ion, this ion will not lose its charge and separate at the electrode in any quantity. Every ion has its own decomposition value, and these values differ very considerably for different ions.

The fact that these values are quite different makes it possible to effect an electrolytic separation of many metals by at first using a current of small electromotive force, which will cause the element with lowest decomposition value to separate, then increasing the electromotive force until the element with next higher value separates, and so on. Take two metals A and B, and mix solutions of their salts. Let the decomposition value of A be considerably less than that of B. Pass a current through the solution containing the mixed salts. When the electromotive force of the current has reached the decomposition value of A, this metal will separate on the cathode. The current will then cease to flow continuously unless its electromotive force is increased to the decomposition value of B. When it has reached this value, B will separate from the solution.

The possibility of thus separating metals by means of currents of different electromotive force was pointed out first by Freudenberg.[1] In an investigation[2] in Ostwald's laboratory, carried out with Le Blanc, Freudenberg effected a number of quantitative separations of metals by using different electromotive forces. Thus, he showed that mercury could be separated from copper, bismuth, arsenic, cadmium, etc.; that copper could be separated from cadmium, and so on. The importance of the electromotive force of the current used is, therefore, very great in effecting electrolytic separation of the metals.

It has, however, been clearly recognized that current strength or current density[3] is of fundamental importance in electrolytic separations. This conditions the number of ions which will separate in a given time; and if the density is great it does not give time for all the more easily discharged ions to come over to the pole by diffusion, etc., in order to separate. Under such conditions, instead of effecting complete separations, only partial separations are secured.

It is obvious from the above that in all such work we must take into account not only current density, but the electromotive force of the current used.

Electrosynthesis of Organic Compounds. — The ions of inorganic compounds are relatively simple substances. The ions of organic compounds are often very complex, and after losing their charge are incapable of existence. They frequently break down and yield entirely new substances. Take the anion of acetic acid, $CH_3\bar{C}OO$, when this reaches the anode it loses its charge, since it holds it less firmly than hydroxyl, and then breaks down in the sense of the following equation: —

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[1] *Ber. d. chem. Gesell.* **25**, 2492 (1892).

[2] *Ztschr. phys. Chem.* **12**, 97 (1893).

[3] Classen: *Quantitative Chemical Analysis by Electrolysis.*

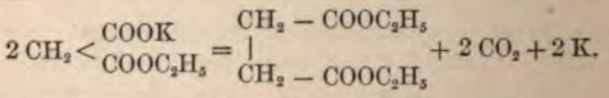
$$2\,\mathrm{C\bar{H}_3CO_2} = \mathrm{C_2H_6} + 2\,\mathrm{CO_2},$$

yielding a hydrocarbon and carbon dioxide. The anion of propionic acid breaks down as follows: —

$$2\,\mathrm{C_2\bar{H}_5CO_2} = \mathrm{C_2H_5COOH} + \mathrm{C_2H_4}.$$

Facts of this kind have already been utilized quite extensively for effecting the synthesis of organic compounds. An examination of the literature[1] will show that a very large number of organic compounds in the aromatic series, as well as in the aliphatic, have been made in this way.

That acetic acid when electrolyzed breaks down as shown in the above equation, yielding ethane and carbon dioxide, had been shown by Kolbe[2] as early as 1847. Some nine years later Guthries[3] showed the inactivity of the ester group. These investigations were the basis of the systematic work of Crum-Brown and Walker[4] in this field in 1891. They showed that from the monoester of a dibasic acid, the ester of a dibasic acid richer in carbon could be obtained. Thus: —



$$2\,\mathrm{CH_2}<\begin{matrix}\mathrm{COOK}\\ \mathrm{COOC_2H_5}\end{matrix} = \begin{matrix}\mathrm{CH_2 - COOC_2H_5}\\ |\\ \mathrm{CH_2 - COOC_2H_5}\end{matrix} + 2\,\mathrm{CO_2} + 2\,\mathrm{K}.$$

The diester of succinic acid is thus prepared from the monoester of malonic acid.

Working with currents of considerable density in fairly concentrated solutions, they effected a number of similar syntheses. Suberic acid was prepared from potassium ethyl glutarate, sebasic acid from potassium ethyl adipate, and so on. The electrical synthesis of organic compounds promises much in the future.

BATTERIES IN GENERAL USE

Primary and Secondary Cells. — This chapter on electrochemistry should not be closed without brief reference to certain forms of batteries which have come into general use as means of furnishing electrical energy. The elements whose electromotive force we have studied are *constant*. The primary cells which are used in practice do not have constant electromotive force, and, therefore, belong to the class of *inconstant* elements. Two of these we shall consider. The bichromate cell and the Leclanché cell. We shall then refer briefly to accumulators or secondary batteries.

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[1] The student is referred in this connection to the admirable little book by Löb on *Electrolysis and Electrosynthesis*, translated by Lorenz.

[2] *Lieb. Ann.* **64**, 236 (1848).

[3] *Ibid.* **99**, 65 (1856).

[4] *Ibid.* **261**, 107 (1890); **274**, 41 (1893).

The Bichromate Cell. — A form of primary element quite frequently used in the laboratory is known as the bichromate cell. The electrodes are carbon and zinc, and the electrolyte chromic acid (potassium bichromate and sulphuric acid). Zinc ions pass into solution, consequently this is the anode. The ions Cr_2O_7 probably yield a few chromium ions of high valence. These pass over into chromium ions of lower valence, and thus add to the electromotive force of the element. It is obvious that the electromotive force of this element cannot remain constant for any length of time, since the Cr_2O_7 ions are continually decreasing in number, the chromium ions of lower valence increasing in number, and the zinc ions are also increasing in number.

The Leclanché Element.[1] — The poles of this useful element are carbon and manganese dioxide, and zinc; the electrolyte ammonium chloride. The carbon and manganese dioxide are generally mixed with each other. Zinc ions pass into solution and, consequently, the zinc pole is the anode. The ammonium ions ($\overset{+}{N}H_4$) pass over to the cathode, but the hydrogen ions already present as the result of the dissociation of water, lose their charge more readily than ammonium, and consequently separate at the carbon cathode. The carbon pole would absorb a large amount of hydrogen.

The MnO_2 acts, as we would expect, as an oxidizing agent. This yields a few $\overset{++++}{Mn}$ ions, which tend to pass over into $\overset{++}{Mn}$, by giving up part of their charge to the cathode. We have thus two actions taking place in the Leclanché element, but the electromotive force decreases because the zinc ions become more and more concentrated.

Accumulators or Secondary Batteries. — Primary cells in which electrical energy is generated directly from heat or from chemical energy have been largely replaced in recent times by accumulators, in which electrical energy is converted into chemical, and this can be reconverted again, at will, into electrical. Theoretically, any reversible element can be made an accumulator by passing a current through it in the direction opposite to that in which the normal current from the element would flow. The accumulators which are used in practice consist of plates of lead covered with a layer of lead oxide or sulphate. The electrolyte is a solution of sulphuric acid, having the specific gravity 1.2. When a current is passed through such a cell, lead dioxide is deposited on the pole where the current enters, and lead is deposited on the other pole. The chemical action of the charging current is to convert lead oxide or sulphate into the dioxide at one pole, and into metallic lead at the other. When the charging current is broken and the cell allowed to discharge, both the lead dioxide and the metallic lead pass over into sulphate. The chemical action when the cell is discharging is, therefore, exactly the opposite of that which takes place when the cell is being charged.

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[1] See also *Outlines of Electrochemistry*, by Jones (Elec. Rev. Pub. Co.).

The chief source of the electromotive force in a secondary battery is the transformation of quadrivalent lead ions $(\overset{++++}{\mathrm{Pb}})$ into bivalent $(\overset{++}{\mathrm{Pb}})$. The quadrivalent ions are furnished continually by the lead dioxide. These pass into bivalent ions and form with the $\overset{=}{\mathrm{SO}_4}$ ions, lead sulphate. At the anode metallic lead passes over into $\overset{++}{\mathrm{Pb}}$ ions, thus removing positive electricity from this pole. These also form with the ions $\overset{=}{\mathrm{SO}_4}$ lead sulphate.

CHAPTER VIII

PHOTOCHEMISTRY

ACTINOMETRY

Transformation of Radiant Energy into Chemical. — We have daily illustrations of the transformation of chemical energy into radiant. In an ordinary flame this transformation is taking place to some extent. The reverse transformation of radiant energy into chemical is also well known, and forms the subject-matter of this chapter.

The action of light on certain silver salts was recognized as early as 1727 by Schultze, but that different kinds of light have different effects was first proved by Scheele in 1777. He exposed paper covered with silver chloride to different parts of the spectrum, and observed that the paper was blackened most rapidly in the violet portion of the spectrum. The time required to color the paper was greater and greater as the red end of the spectrum was approached.

This action of light on silver salts was utilized by Daguerre in 1839 for obtaining images of objects, and thus was started the science of photography.

We know to-day that the transformation of radiant energy into chemical depends largely upon the wave-length of the former. Certain photochemical reactions are produced most vigorously by the violet and ultra-violet rays, while others are chiefly effected by the longer wave-lengths. Thus, as we have seen, the halogen salts of silver are acted upon most vigorously by the shorter wave-lengths; while the transformation of radiant energy into chemical, which is going on in plants, attains a maximum in the yellow portion of the spectrum.

Some of the more important generalizations[1] which have been reached in reference to the chemical action of the solar spectrum are the following: —

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[1] Eder: *Fehling's Handwörterbuch der Chemie,* Vol. IV, pp. 124–125 (1886). *Licht; Chemische Wirkungen.*

1. "Light of every color from the extreme violet to the extreme red, and also the invisible ultra-red and ultra-violet rays, can produce chemical action."

2. "All rays which act chemically on a substance must be absorbed by it; the chemical action of light is closely connected with optical absorption."

3. "Every color of the spectrum can have an oxidizing and a reducing action, depending upon the nature of the substance which is sensitive to the light."

Actinometers. — The measurement of the intensity of the actinic rays is based upon the chemical transformation which they can effect. A number of forms of apparatus have been devised for measuring the photochemical action of light. These are known as *actinometers*. The *hydrogen-chlorine* actinometer is based upon the fact discovered in 1809 by Gay-Lussac and Thénard, that light has a marked influence on the union of these two gases. Draper[1] constructed an actinometer in which these two gases were used, but this was so greatly improved by Bunsen and Roscoe,[2] whose work in this field was of fundamental importance, that we will turn our attention at once to their apparatus.[3] The glass tube, Fig. 54, is filled with a mixture of equal parts of hydrogen and chlorine, obtained by electrolyzing a solution of hydrochloric acid of specific gravity 1.148, using carbon electrodes. The lower blackened portion of *i* contains water. This is connected at one end with a tube closed by a stopcock, *h*, and at the other with a tube, *k*, which is connected with a vessel, *l*, filled with water. After the liquids have become saturated with the mixture of gases, *h* is closed, and the whole tube protected from the light except the bulb *i*. The light is now allowed to fall on this bulb, when some of the gases combine, forming hydrochloric acid. The latter is absorbed by the water in *i*, and the column of water moves from *l* along the graduated tube *k*. By this means the amount of gases which have combined is readily determined, and from this the intensity of the photochemical action. If the light is too strong, explosions may result in this form of actinometer. To avoid this Burnett[4] replaced the hydrogen of the mixture by carbon monoxide.

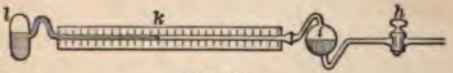

Fig. 54.

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[1] *Phil. Mag.* [3], **23**, 401 (1843).

[2] *Pogg. Ann.* **100**, 43 (1857); **101**, 235 (1857); **108**, 193 (1859).

[3] *Ibid.* **100**, 43 (1857).

[4] *Phil. Mag.* [4], **20**, 406 (1860).

Bunsen and Roscoe[1] used later the *silver chloride* actinometer. This depends upon the time required to produce a given color in silver chloride paper. The intensity of the light varies inversely as the time.

A number of other chemical reactions which are effected by light, have been used to measure the intensity of the light. The action of mercuric chloride on ammonium oxalate takes place in the presence of light in terms of the following equation: —

$$2\ HgCl_2 + (NH_4)_2C_2O_4 = 2\ NH_4Cl + 2\ CO_2 + 2\ HgCl.$$

The amount of decomposition can be readily determined by weighing the amount of mercurous chloride formed. The amount of mercurous chloride formed increases more slowly than the intensity of the light, since the mercuric chloride in the solution is continually becoming less. This necessitates the introduction of a correction which has been worked out by Eder.[2]

Instead of mercuric chloride and oxalic acid Niepce de St. Victor used oxalic acid and uranium nitrate, and Draper used ferric oxalate.

Certain forms of *electrical actinometers* have been discovered and used. Becquerel[3] found that when two plates of silver covered with silver iodide are immersed in water containing an acid, and light is allowed to act on one electrode, a current is set up between the plates. From the electromotive force of this combination the amount of the chemical action produced, and, consequently, the intensity of the action of light, can be determined. A number of modifications of this electrochemical actinometer have been proposed. Grove[4] used platinum plates in dilute sulphuric acid, and Gouy and Rigollet[5] employed strips of copper covered with a thin layer of copper oxide, immersed in a one-tenth per cent solution of sodium chloride, bromide, or iodide.

Ostwald[6] offers the following explanation of the action of the Becquerel actinometer: "Silver iodide is rendered less stable by the action of light, and breaks down into its ions silver and iodine. The silver ions give up their charge to the metal and separate upon it as metallic silver, the iodine ions passing into solution. From the pole which has not been exposed to light a corresponding number of silver ions separate, thus rendering this pole negative. This explanation accords with the fact that in such an actinometer the current flows on the outside from the pole which has been exposed to the action of light."

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[1] *Pogg. Ann.* **117**, 529 (1862); **124**, 353 (1865); **132**, 404 (1867).

[2] *Wiener. Ak. Sitzungsber.* [2], **80**, Okt. (1879).

[3] *Compt. rend.* **9**, 561; **13**, 198. *Ann. Chim. Phys.* [3], **9**, 257 (1843); [3], **32**, 176 (1851).

[4] *Phil. Mag.* [4], **16**, 426 (1858).

[5] *Compt. rend.* **106**, 1470 (1888). *Ann. Chim. Phys.* [6], **22**, 567.

[6] *Lehrb. d. Allg. Chem.* II, 1043.

RESULTS OF PHOTOCHEMICAL MEASUREMENTS

Photochemical Extinction. — Bunsen and Roscoe[1] undertook to decide whether in photochemical action work is done for which an equivalent amount of light disappears, or whether there is an action produced by the chemical rays without any considerable loss in light. They passed light through a layer of a mixture of hydrogen and chlorine, and determined the loss in chemical activity by the hydrogen chlorine actinometer. They then passed light through an equal layer of chlorine and determined the loss. The loss in the first case was greater than in the second. In the second case there was simply the optical absorption of the chlorine, the light energy which disappeared being converted into heat. In the first case there was the optical absorption of the chlorine and of the hydrogen, and in addition a certain amount of light was expended in doing chemical work. Since the optical absorption of hydrogen can be disregarded, the difference between the light which disappeared in the first and second cases can be taken as the amount expended in doing chemical work.

From the work of Bunsen and Roscoe it follows that about *one-third* of the light absorbed from a gas-flame by a mixture of hydrogen and chlorine is expended in doing chemical work, while the remaining two-thirds is converted into heat. The ratio between these quantities varies greatly with the nature of the light which is employed.

Against this conclusion of Bunsen and Roscoe, E. Pringsheim[2] makes the following point: The light absorbed by pure chlorine is converted into heat, but when the chlorine is mixed with hydrogen it is very probable that the light absorbed is used up wholly or largely in doing chemical work.

Photochemical Induction. — The discovery was made by Becquerel,[3] in 1843, that while silver chloride which had not been exposed to light was sensitive only to the short wave-lengths of light, silver chloride which had been exposed a short time to light, but which had not darkened, was sensitive also to the longer wave-lengths. The former was acted upon only by wave-lengths shorter than the green, while the latter was sensitive even down into the ultra-red. Differences of the same kind were observed with other substances.

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[1] *Pogg. Ann.* **101**, 235 (1857).

[2] *Wied. Ann.* **32**, 386 (1887).

[3] *Ann. Chim. Phys.* [3], **9**, 257 (1843).

Similar phenomena were studied quantitatively by Bunsen and Roscoe,[1] who used the term *photochemical induction.* They allowed light from a constant source to pass through a mixture of hydrogen and chlorine, which had been freshly prepared or had stood for a considerable time in the dark. At first there was little or no action. After some time a slight action began, and this increased gradually up to a constant maximum value. The following results taken from the paper[2] of Bunsen and Roscoe will make this clear. The first column gives the time in minutes, the second the amount of hydrochloric acid formed during each minute, as measured by absorption in water and the movement of the water column in the actinometer. The source of light was the zenith of a clear sky.

TIME IN MINUTES	AMOUNT HCl FORMED	TIME IN MINUTES	AMOUNT HCl FORMED
1	0.0	7	2.2
2	0.0	8	1.7
3	0.9	9	3.0
4	1.0	10	5.2
5	1.3	11	5.8
6	2.0	12	5.7

The maximum value was reached after about eleven minutes. They also studied the action of lamplight, and found that from nine to fifteen minutes were required for the action to reach a maximum constant value.

After the action had reached a maximum the mixture of gases was placed in the dark, and it was found that after a half-hour the gases were in the same condition as they were before exposure to light. It now required about the same exposure to bring the action again up to the maximum value.

If the gases are exposed separately to the light and then mixed, the action does not attain a maximum at once, but it requires about the same time for an appreciable action to begin and for the maximum to be reached, as if the gases had been kept in the dark. The first action of the light, whatever it may be, therefore takes place only when the molecules of the two gases are in the presence of each other.

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[1] *Pogg. Ann.* **100**, 481 (1857).

[2] *Ibid.* **100**, 484 (1857).

Some suggestions have been made to account for photochemical induction. E. Pringsheim[1] thinks that in the action of light on hydrogen and chlorine an *intermediate product* is formed. He was led to this conclusion from his elaborate study of this reaction, but the point cannot be regarded as proved.

The Action of Light on Certain Silver Salts. — The action of light on certain salts of the heavy metals, and especially of silver, has become of the very greatest importance not only from a practical standpoint, but from a scientific. The science of photography is based upon this action, and there are few branches of science into which photography has not entered as a very important factor.

On the photographic plate the silver salt is exposed to the action of light, but not until any visible change has taken place. The plate is then treated with the developer, which reacts with different velocities upon the parts which have been exposed to lights of different intensities. The result is an image of the object from which the light came.

The Action of Light in the Formation of Isomeres and Polymeres. — In connection with the action of light in the formation of *isomeric* substances, we think first of the action of bromine on toluene. If the reaction takes place in the dark or in diffused light, there is formed, as Schramm[2] pointed out, a mixture of ortho- and parabromtoluene $C_6H_4Br.CH_3$. But if the reaction takes place in the direct sunlight, the isomeric benzyl bromide $C_6H_5.CH_2Br$ is formed.

There are a number of acids known which are transformed by light into *stereoisomeric* substances, as Liebermann[3] has shown; and J. Wislicenus[4] has pointed out a number of other cases, such as the transformation of maleïc into fumaric acid, and of angelic into tiglic acid. From these observations Roloff[5] draws the following conclusions: Light always transforms from a *malenoid* to a *fumaroid* form; the transformation takes place with an *evolution of heat*, and, therefore, gives rise to more stable forms.

Roloff[6] points out a number of examples where light acts as a polymerizing agent, after showing how we can distinguish between a metamer and a polymer. We may mention the transformation of yellow into red phosphorus, of monoclinic into amorphous sulphur, of amorphous into crystalline selenium, of the aldehydes into polymeres, of acetylene into benzene, and many other examples could be cited.

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[1] *Wied. Ann.* **32**, 384 (1887).

[2] *Ber. d. chem. Gesell.* **18**, 350, 606 (1885); **19**, 212 (1886). *Monatsh.* **8**, 101 (1887); **9**, 842 (1888).

[3] *Ber. d. chem. Gesell.* **28**, 1443 (1895).

[4] *Sachs. Ber.* 489 (1895).

[5] *Ztschr. phys. Chem.* **26**, 339 (1898).

[6] *Ibid.*

The Law of Photochemical Action. — One generalization of considerable value has thus far been reached as the result of the work done in the field of photochemistry. Bunsen and Roscoe[1] showed experimentally, in their now classical investigations in this field, that photochemical action is proportional to the intensity of the light and to the time which it acts. They studied the time required to produce a given blackening of silver chloride by light varying in intensity from one to twenty-five, and concluded that whenever the product of the intensity and time of exposure is a constant the same blackening is produced. The law then is, *that photochemical action is equal to the product of the intensity of the light and the time during which it acts.* This is the same as to say that a given photochemical effect is produced by a given number of vibrations, independent of the time required to receive them.

PHOTOCHEMICAL ACTION OF NEWLY DISCOVERED FORMS OF RADIATION

The Röntgen Rays. — An observation was made by Röntgen which led him in 1895 to one of the most important discoveries[2] in modern physics. When the discharge from an induction coil is passed through a Crookes or Lenard tube of sufficient exhaustion, the tube being completely covered with black paper and placed in a dark room, there is produced a bright illumination on paper covered with barium platinocyanide. The fluorescence was visible even when the screen was placed at a distance of two metres from the tube.

As Röntgen states, the most striking property of this radiation is that it passes through substances which are opaque to visible and ultra-violet rays. Paper and wood are very transparent, and most of the metals allow the radiation to pass through to a considerable extent. The metals, however, differ very considerably in their transparency to this radiation. Some fluorescence was produced when a screen of aluminium 15 mm. thick was interposed, while a plate of lead 1.5 mm. thick is practically opaque. Platinum is among the more opaque metals. The opacity of substances to this radiation is conditioned chiefly by their atomic weight, but this is not the only factor, since different substances of the same density have different degrees of opacity.

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[1] *Pogg. Ann.* **117**, 529 (1862).

[2] *Sitzungsber. Würzb. phys. medicin. Gesell.* 1895. *Wied. Ann.* **64**, 1 (1898).

This form of radiation produces fluorescence not only in barium platinocyanide, but also in phosphorescent calcium compounds,— calcite, uranium glass, etc.; and also produces chemical action on photographic dry plates, either directly or by means of the fluorescent light set up in the glass or film.

Röntgen showed that this radiation comes from the place where the cathode rays strike the glass of the exhausted tube, that it could not be reflected, refracted, or polarized, and that it ionized gases through which it passed; therefore, differs fundamentally from cathode rays. This radiation also differs fundamentally from ultra-violet light. Röntgen thought that this radiation was produced by *longitudinal vibrations* in the ether.

A very different view as to the nature of the Röntgen ray is held by Stokes.[1] He recognizes that these rays must be something propagated in the ether, and are produced by the cathode rays striking upon the glass walls of the exhausted tube. The cathode rays are streams of highly charged particles. These fall upon the walls of the vacuum tube, and each molecule sets up a *pulse* in the ether. The Röntgen ray is then a vast succession of these *independent pulses*, sent out in an irregular manner.

By means of this theory Stokes shows that he can explain the facts which are known in a perfectly satisfactory manner. Their penetrating power is due to the fact that the pulse is gone before any harmonious vibration between the ether and the molecules can be set up. This theory also accounts for the absence of diffraction more satisfactorily than by assuming that the Röntgen rays are rays of light of very short wave-length. The view of Stokes supported by J. J. Thomson[2] is the one now generally accepted.

The Becquerel Rays.—A form of radiation which in some respects resembles the Röntgen rays, but in others seems to differ from it, was discovered by Becquerel[3] in 1896. Compounds of uranium when exposed to light have the property of emitting an invisible radiation which traverses many substances impervious to light, such as black paper, thin sheets of many metals, such as aluminium, copper, etc. This property is possessed by metallic uranium to from three to four times the extent that it is manifested by the salts of this metal.

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[1] *Manchester Lit. and Phil. Soc.* **41,** Part IV, 1896–1897. Scientific Memoirs Series, III, 43. "The Wilde Lecture," July 25, 1897.

[2] *Phil. Mag.* **45,** 172 (1898).

[3] *Compt. rend.* **122,** 420, 501, 559, 589, 762, 1086; **123,** 855; **124,** 438, 800; **128,** 771; **129,** 912; **130,** 206, 372, 809, 979, 1154; **131,** 137; **132,** 371 (1896–). *Nature*, **63,** 396 (1901).

This is entirely different from the phosphorescence shown by salts of uranium, since the latter disappears very quickly, while the power of emitting this invisible radiation persists for years.

If a piece of uranium or of one of its salts is placed above a photographic plate covered with black paper or aluminium leaf, and various substances are interposed between the uranium and the plate, after several hours "radiographs" are obtained upon the plate. These rays were also supposed for a time to be capable of polarization by means of tourmalines. These phenomena would suggest properties analogous to those possessed by light, and led Stokes[1] to conclude that the Becquerel rays occupy a position intermediate between the Röntgen rays and light. As we have seen, he regarded the Röntgen ray as made up of a great number of independent pulses. In the Becquerel ray he thought that there was still irregularity, but some regularity was beginning to manifest itself.

Later experiments, however, have shown that the uranium radiation undergoes neither reflection, refraction, nor polarization.

This radiation is transmitted differently through screens of different substances, depending upon the angle in which they are simultaneously placed in the path of the radiation. This would indicate that the radiation is not homogeneous.

The uranium radiation discharges positive and negative charges with equal speed, and its power to render a gas a conductor has been shown by Rutherford[2] to be due to an ionization of the gas. The above and similar phenomena have been characterized as *radioactivity*.

Other Radioactive Substances. — The discovery was made in 1898 by G. C. Schmidt[3] that thorium, like uranium and its compounds, can send out rays which are similar to the Röntgen rays. A little later (1898) M. and Mme. Curie[4] observed that certain uranium minerals, such as pitchblende, were radioactive to a much greater degree than metallic uranium or thorium. The conclusion was drawn that in such minerals there are other radioactive substances than uranium, and an attempt was made to isolate such substances. Pitchblende was dissolved in acid, and hydrogen sulphide passed into the solution. The sulphide of the active substance is insoluble in ammonium sulphide, and was partially separated from the other sulphides insoluble in this substance. Further, when the mixed sulphides from pitchblende are heated to 700°, the active substance sublimes into the cooler portion of the tube. The substance obtained in this way was 400 times as active as uranium. This was further purified by removing the bismuth until a much greater radioactivity was shown. This substance was called *polonium,* after the native country of Mme. Curie.

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[1] *Loc. cit.*, "Wilde Lecture.

[2] *Phil. Mag.* **47**, 109 (1899).

[3] *Wied. Ann.* **65**, 141 (1898).

[4] *Compt. rend.* **127**, 175 (1898).

M. and Mme. Curie[1] discovered a second radioactive substance in pitchblende. This substance is obtained with the barium, from which it is impossible to effect a complete separation. This substance is not precipitated by hydrogen sulphide nor ammonium sulphide. By dissolving the chloride in water and precipitating with alcohol, a substance was obtained which had a radioactivity 17,000 times that of uranium. This substance they termed *radium.* The spectrum was determined by Demarcay,[2] and new lines were discovered.

More recently Debierne[3] claims to have discovered a third radioactive substance in pitchblende, which is closely allied to titanium in its properties.

The rays from radium are much more intense than those from polonium, uranium, or thorium. Rays from radium and polonium produce fluorescence in barium platinocyanide, while those from thorium and uranium are not sufficiently intense to excite this fluorescence. The radiation from polonium is much less penetrating than that from radium, not being able to traverse even black paper.

The rays from certain radiating substances are deviated by a magnetic field, while other rays are not deviated. This shows that there are two kinds of rays given out by radioactive substances; indeed, both kinds coexist in the radium radiation. The nature of the kind which cannot be deviated is unknown, and these are much less penetrating than the deviable rays, which have been shown to be identical with the cathode rays. It has also been shown that in the radium radiation there are very penetrating rays which are not deviable.

In identifying the deviable rays with cathode rays it has been demonstrated that there is a transport of electrical charges and also a deviation in an electrostatic field. By comparing the electrostatic and electromagnetic deviations the velocity of the particles was determined and found in one case to be 1.6×10^{10}, or about one-half that of light. The ratio of the masses to the charges which they carry was shown to be 10^{-7}, which corresponds exactly to the cathode ray.

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[1] *Compt. rend.* **127**, 1215 (1898). *Chem. News*, **79**, 1 (1899).

[2] *Ibid.* **127**, 1218 (1898).

[3] *Compt. rend.* **129**, 593 (1899).

From the above and other data it has been calculated that the loss of matter from each square centimetre of surface of the radioactive substance is one milligram in about one thousand million years. As Becquerel[1] says, "If the material emission, which appears to be of the same order as the evaporation of certain scented substances, is the first cause of the observed phenomena, there would be no contradiction between the apparent absence of any source of energy and the continuous emission of this energy."

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[1] *Nature*, **63**, 398 (1901).

CHAPTER IX

CHEMICAL DYNAMICS AND EQUILIBRIUM

HISTORICAL SKETCH

Earlier Views. — The fact that different forms of matter can combine with one another, giving new products, was recognized as early as chemical elements and compounds were dealt with. Certain elements combine with certain other elements giving compounds many of whose properties differed fundamentally from those of either element. Some elements combine with the greatest ease, evolving a large amount of heat, while others combine with difficulty, or only at elevated temperatures, while others again would not combine under any known conditions. It was also early observed that one element may have the power of breaking down a compound containing two or more elements, combining with one or more elements and setting the remainder free. It was, therefore, obvious that elements possess very different powers of combination, and that the compounds formed have very different degrees of stability.

The property of elements to enter into chemical combination was named *chemical affinity*. The earlier experimenters and observers, however, were not content with merely naming the phenomena, but sought to explain it, and a number of theories were proposed quite early to account for chemical union. Passing over certain metaphysical speculations of the Greeks, which referred chemical union to love and decomposition to hate between the atoms, and certain mechanical conceptions of chemical union, which regarded the atoms as provided with hooks which interlocked and formed chemical compounds; we come to the time of Newton. His discovery of the law of gravitation seemed to throw new light on the problem of chemical affinity. If large masses of matter attract one another proportional to the product of their masses and inversely as the square of the distance, why might not the attraction between atoms follow the same law? In a word, why might not chemical attraction and the attraction of gravitation be referred to the same cause?

Although Newton showed that chemical attraction decreases more rapidly with the distance than would be required by the law of gravitational attraction, yet Buffon and others were deeply influenced by the discovery of Newton, in their attempts to explain chemical attraction.

At the beginning of the nineteenth century an entirely new conception was introduced in the attempts to explain chemical attraction. The power of the electric spark to effect both chemical union and decomposition was known. Cavendish showed that nitric acid is formed from air when electric sparks are passed through it, and Priestley found that ammonia was decomposed by the electric spark into products whose volume was greater than its own. The discovery of Galvani, and the utilization of this discovery by Volta in the construction of his pile, gave a continuous supply of electricity on a comparatively large scale. It was quickly discovered that the electric current can not only decompose water, but also many other chemical compounds, such as salts of the heavy metals. Since chemical attraction could be so readily overcome by the current, it seemed probable that there was a very close relation between chemical attraction and electrical attraction. As the result we have the electrochemical theories of Davy and Berzelius to which sufficient reference has already been made. The fundamental conception which underlies both of these theories is that chemical attraction is nothing but the electrical attraction of oppositely charged parts.

The earlier chemists were not content with theorizing about the nature of chemical affinity, but carried out elaborate experimental investigations in which they measured the relative affinities of substances for one another. To some of the more important of these we shall now turn.

Geoffroy's and Bergmann's Tables. — Geoffroy attempted to arrange chemical substances in tables in the order of their affinity. A given substance was placed at the top of a table, and other substances arranged in the order of their decreasing affinity for the substance in question. The substance higher in the table displaced from their compounds those below it, the ease with which the displacement took place depending upon the relative positions in the table. This method of dealing with chemical affinity referred it entirely to the nature of the substances which were brought together, and made it independent of any external conditions to which the substances were subjected.

Bergmann went much farther than Geoffroy in that he recognized that the power of substances to react chemically depended not only upon their nature, but also upon other conditions. Thus, the state of division had a marked influence on the reactivity of substances, and this explained why substances react much better in solution than in the solid state. The table expressing the relative affinities of substances in the dry state would thus be very different from the table for the same substances in solution. We would, therefore, have two tables of affinity, — one in the dry state and one in the wet. Bergmann pointed out that these tables of affinity are purely qualitative, representing the relative affinities of substances for one another. They were not to be regarded as a quantitative expression of the magnitude of chemical attraction between substances, since this varies so greatly with the conditions.

One point of fundamental importance as conditioning chemical activity was overlooked by Bergmann, *i.e.* the effect of mass. It remained for Wenzel to point this out.

Wenzel points out the Effect of Mass. — In his book,[1] published in 1777, Wenzel dealt with the whole problem of chemical action in a much broader way than any one had done up to his time. He considered the various influences which might come into play to account for chemical action, and observed certain discrepancies which could not be accounted for by any of the ordinary methods. Thus, under some conditions sulphuric acid will replace nitric acid from its salts; under other conditions nitric acid will replace sulphuric. This led Wenzel to inquire into the effect of different quantities of one substance with respect to the other on the velocity and the amount of the reaction between the two. He was led to the conclusion that chemical action is proportional to the concentration of the substances entering into the reaction. This was the first recognition of the effect of mass on chemical action.

The Work of Berthollet. — The first systematic experimental study of the effect of mass on chemical action was made by Berthollet[2] at the very beginning of the nineteenth century. His first paper was published in 1799 while with Napoleon in Cairo; Berthollet having been selected as one of several men of science to accompany Napoleon on his Egyptian expedition. The views of Berthollet in reference to the effect of mass on chemical action are clearly expressed in this first communication.[3]

Chemical affinities do not act as absolute forces, by means of which one substance can replace another from its compounds; but in all combinations and decompositions we must take into account not merely the strength of the affinities, but also the *masses* of the substances which are reacting. The effect of mass can overcome the force of affinity, from which it follows that the activity of a substance must be measured by the mass which is required to bring about a definite degree of reactivity.

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[1] *Lehre von der chemischen Verwandtschaft der Körper.*

[2] *Essai de Statique Chimique.* Papers compiled in *Ostwald's Klassiker der Exakten Wissenschaften*, No. 74.

[3] *Ostwald's Klassiker*, **74**, 5.

Berthollet carried out a number of experiments, which he described in a second[1] communication, showing the effect of mass action. Barium sulphate was decomposed by potassium hydroxide, the amount of the decomposition depending upon the amount of the hydroxide present. Similarly calcium oxalate was decomposed by potassium hydroxide in varying amounts, depending upon the quantity of the hydroxide used. It is possible to effect almost complete decomposition of the sulphate and oxalate if enough hydroxide is used.

Berthollet studied also the effect of solubility on chemical activity. In order that substances may react there must be good contact, and such is established in solution. Substances react not according to the total amount present, but according to the amount in solution. This appeared in his fourth communication. In subsequent papers he took up the study of the nature of the solvent, the effect of heat, etc., on chemical action; but the essential features in his theory of mass action were presented in his earlier communications. The views of Berthollet are summarized by himself[2] as follows, "The chemical activity of a substance depends upon the force of its affinity and upon the mass which is present in a given volume."

The theory of Berthollet was not immediately accepted. Indeed, for a considerable time it exercised very little influence on chemical thought. It appeared to thinking chemists that Berthollet had gone too far in supposing that mass was the chief factor in conditioning chemical activity. The opposition to, or neglect of, his views was increased by a conclusion to which he thought himself forced by his discoveries. If reaction depends chiefly upon mass, then the quantity of one substance which combines with a given quantity of another substance should depend upon the relative masses of the substances which are present. This was directly at variance with the idea of the constant composition of chemical compounds, and led to the classical discussion between Proust and Berthollet. The well-known result was that Berthollet was in error in this conclusion, the work of Proust showing that Dalton's laws of constant composition and multiple proportion were undoubtedly correct. All this tended to bring Berthollet's generalization into disrepute, and the effect of mass as playing any prominent rôle in chemical reactions was almost entirely disregarded for forty years. It was, however, again brought to the front in 1842 by the work of Rose.

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[1] *Ostwald's Klassiker*, **74**, 7.

[2] *Ibid.* **74**, 70.

The Observations of Heinrich Rose. — Rose showed that the sulphides of the alkaline earths are decomposed by water yielding the corresponding hydroxides, the amount of the decomposition depending upon the amount of water present.

He also called attention to a phenomenon in nature which illustrates in a striking way the action of mass. The silicates are among the most stable compounds known, being decomposed with any considerable velocity only by the most powerful chemical reagents. Yet in nature these compounds are undergoing continual decomposition, which is effected by such weak reagents as carbon dioxide and water. All over the surface of the earth we have the transformation of silicates into carbonates, due to the action of the enormous amounts of carbon dioxide in the air and water. This reaction cannot be effected to any appreciable extent in the laboratory, since the time at disposal for such an experiment is not sufficiently great. Here we have, then, a beautiful example of the effect of mass on chemical activity.

One other example which was pointed out by Rose should be cited. When a boiling solution of acid potassium sulphate of medium concentration is crystallized, the crystals have the composition expressed by the formula $3\ K_2SO_4\ H_2SO_4$ and water, a portion of the sulphuric acid having been split off to combine with the water. If these crystals are redissolved in more water, and the solution evaporated to crystallization, the neutral salt will separate, showing a further splitting off of sulphuric acid due to the mass action of the water.

These examples and many others, which were brought forward by Rose, called attention again to the importance of mass as conditioning chemical reactions, and succeeded in arousing interest about the middle of the century in the theory which had been advanced by Wenzel and experimentally verified by Berthollet at the beginning.

Renewed Interest in the Theory of Mass Action. — After the above facts had been pointed out by Rose, observations illustrating the effect of mass were made on all sides. Dulong[1] studied quite early the decomposition of barium sulphate by potassium carbonate when the two were fused together, and also when the sulphate was boiled with a solution of the carbonate. The amount of the sulphate transformed into carbonate depends upon the amount of the soluble carbonate present. He also showed that barium carbonate can be transformed into sulphate by boiling with a solution of a soluble sulphate.

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[1] *Pogg. Ann.* [1], **82**, 273 (1812).

Rose[1] studied these reactions quantitatively, and showed that the action of the soluble salt ceases long before it has all been used up. If to a solution of potassium carbonate a certain amount of a soluble sulphate is added, it no longer has the power to transform barium sulphate into carbonate. He observed that strontium and calcium sulphates are more easily decomposed by a soluble carbonate than barium sulphate, and explained this as due to the greater insolubility of the barium sulphate. He supposed, and correctly, that the soluble sulphate formed would begin to react on the barium carbonate, giving the very insoluble barium sulphate.

That such a reaction as the above is reversible, was pointed out clearly by Malaguti.[2] He showed that we have to deal here with two reactions, — the one giving barium carbonate and potassium sulphate, and that these then react, giving again barium sulphate and potassium carbonate. As the amount of potassium sulphate present increases, the velocity of the second reaction increases, until finally the velocities of the two opposite reactions become equal. At this point we have the maximum amount of decomposition of the barium sulphate, which, under the conditions, it is possible to obtain.

Malaguti carried out a large number of experiments on the decomposition of insoluble salts by soluble, but failed to reach any very wide generalization.

The Law of Reaction-velocity. — In 1850 Wilhelmy[3] studied the inversion of cane sugar by acids, and discovered one of the most important laws in chemical dynamics. He varied the temperature, the quantity of sugar, the quantity of acid, and used different acids. He arrived at the result that *the amounts transformed in a given time are proportional to the amounts present at that time.*

If both substances undergo change, the velocity is proportional to the product of the two active masses. Since, however, in the case of the inversion of cane sugar by acids, only the cane sugar undergoes change, the velocity is dependent only upon the amount of sugar in the solution.

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[1] *Pogg. Ann.* **94**, 481 (1855); **95**, 96, 284, 426 (1855).

[2] *Ann. Chim. Phys.* [3], **51**, 328 (1857).

[3] *Pogg. Ann.* **81**, 413 (1850). *Ostwald's Klassiker*, No. 29.

Wilhelmy[1] formulated these relations as follows: "Let dZ be the amount of sugar inverted in unit time dT, and let us assume that this is given by the formula, —

$$-\frac{dZ}{dT} = MZS,$$

in which M is the mean value of the infinitely small quantity of sugar, which is transformed in unit time by the action of unit quantity of acid. (Z is the amount of the sugar, S that of the acid.)

" The above equation gives on integration, —

$$\log Z = -\int_0^T MSdT;$$

or since, as already shown, S is constant, M on the other hand is independent of Z and, therefore, of T, which should be established later by experiment, —

$$\log Z = -MST + C.$$

$$\text{For } T = 0,\ Z = Z_0,$$

whence, $\log Z_0 - \log Z = MST$, or $Z = Z_0 E$. Since Z_0, S, and T are given, and Z is known by experiment, the formula can be used to determine M."

This work of Wilhelmy must be regarded as the foundation of chemical dynamics. The relation which he established is a general one, holding for the velocity of all reactions in which only one substance is transformed. Wilhelmy recognized that the velocity of the reaction is largely influenced by the nature of the acid used, but did not arrive at any general relation connecting this property of acids with any other properties. Lowenthal and Lenssen[2] took up the latter problem and showed that a very interesting and important relation exists. The velocities with which acids will invert cane sugar are proportional to the strengths of the acids. They pointed out that since this relation exists, the rates at which different acids invert sugar can be used as a ready means of measuring the relative strengths of acids. They determined the relative rates at which a number of the more common acids effect inversion; the halogen acids and nitric acid having the greatest action, while sulphuric, phosphoric, and the organic acids invert much slower.

Work of Berthelot and Péan de Saint Gilles. — Berthelot and Péan de Saint Gilles[3] investigated experimentally the effect of mass on chemical action by studying the formation of ethereal salts from alcohols and acids. This reaction is particularly well adapted to the purpose, since it proceeds slowly and tends toward a limit, the point of equilibrium being determined by the amount of alcohol or acid present, by the temperature, etc. Furthermore, this reaction is reversible, *i.e.* the products of the first reaction react in turn and give rise to the original substances. Thus, an ethereal salt and water react, and give the alcohol and acid from which the ethereal salt was formed.

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[1] *Pogg. Ann.* **81**, 418 (1850).

[2] *Journ. prakt. Chem.* **85**, 321 (1852).

[3] *Ann. Chim. Phys.* [3], **65**, 385; **66**, 5; **68**, 225 (1862–1863).

They found that temperature had a marked influence on the velocity of the reaction, the same amount of ethereal salt being formed in less than five hours at 100°, as was formed in 95 days at from 6° to 9°. Pressure up to 80 atmospheres had no appreciable influence.

Berthelot and Péan de Saint Gilles investigated also the effect of the nature of the acid and of the base on the *velocity* with which the ester is formed, and the *amount* of ester formed when equilibrium was reached. With a given alcohol, the velocity of ester formation decreases as the acid becomes more complex. With a given acid, the velocity of ester formation does not vary appreciably with the complexity of the alcohol. Berthelot[1] concluded from their study of the velocity of ester formation, that the amount of ester formed in every moment is proportional to the product of the masses of the reacting substances, and inversely proportional to the volume, which contains essentially the views which we hold to-day.

From the study of the relation between the chemical composition of the acid and alcohol, and the amount of ester formed, some interesting conclusions were reached. A few of their results are given, in which different alcohols and acids were employed. The reaction was allowed to proceed until the maximum amount of ester was formed under the conditions. The results are expressed in percentage of the theoretical amount of ester which would be formed if the reaction went to the end: —

	ESTER FORMED
C_2H_6O and CH_3COOH	66.9 %
C_2H_6O and $CH_3.CH_2.CH_2COOH$	69.8 %
C_2H_6O and C_6H_5COOH	67.0 %
CH_4O and CH_3COOH	67.5 %
CH_4O and C_6H_5COOH	64.5 %
$C_5H_{12}O$ and CH_3COOH	68.9 %
$C_5H_{12}O$ and C_6H_5COOH	70.0 %

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[1] *Ann. Chim. Phys.* [3], **66**, 110 (1862).

The result is very surprising in that neither the nature of the acid nor the base has any marked influence on the amount of ester formed.

The most interesting question studied by Berthelot and Péan de Saint Gilles still remains. They varied the quantity of alcohol with respect to that of the acid, and noted the effect on the amount of ester formed. The following results were obtained with ethyl alcohol and acetic acid, E representing the number of equivalents of ethyl alcohol to one of acetic acid: —

E	Ester Formed	E	Ester Formed
0.2	19.3 %	4	88.2 %
0.5	42.0 %	12	93.2 %
1.0	66.5 %	19	95.0 %
1.5	77.9 %	50	100.0 %
2.0	82.8 %		

These results show in a most striking manner the effect of mass action. When one-fifth of an equivalent of alcohol is used, only 19.3 per cent of the possible amount of ester is formed. When the alcohol is increased to one equivalent, the amount of ester increases to 66.5 per cent of the possible amount, while an increase in the number of equivalents of alcohol up to fifty transforms all the acid present into ester.

This relation, which is general for different alcohols and acids, shows in a most striking manner the effect of mass on chemical activity. Indeed, few investigations have ever been carried out in which the effect is so satisfactorily demonstrated.

Dissociation by Heat. — It was early known that many complex substances are broken down by heat into simpler parts. Thus, calcium carbonate is decomposed by heat into calcium oxide and carbon dioxide, ammonium chloride is broken down into ammonia and hydrochloric acid. Such phenomena are known as dissociation by heat, to distinguish them from the dissociation effected by solvents like water. Dissociation by heat was studied extensively about the middle of the nineteenth century by Sainte-Claire Deville.[1] He thought that the amount of decomposition is dependent upon the temperature, and introduced the conception of dissociation-tension, which is analogous to that of vapor-tension.

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[1] *Compt. rend.* **45**, 857; **56**, 195, 729; **59**, 873; **60**, 317.

It is a remarkable fact that from his studies of dissociation by heat Deville[1] was led to the conclusion that mass has little or no influence on chemical action. We know to-day that there are few lines of investigation which have pointed so clearly to the effect of mass action. Take the well-known cases of ammonium chloride and phosphorus pentachloride. If ammonium chloride is vaporized it is decomposed to some extent into its constituents, as was shown by the work of Pebal, Than, and others; and also by the fact that its vapor-density is too low. If, however, ammonium chloride is volatilized in an atmosphere of ammonia or of hydrochloric acid, the vapor-density corresponds much more nearly to that calculated from the molecular weight of the compound. This shows that the dissociation is diminished by an excess of either product of the dissociation.

The case of phosphorus pentachloride is even more striking. When this compound is volatilized, it is decomposed to a considerable extent into phosphorus trichloride and chlorine, as was proved by the color of the vapor showing the presence of free chlorine, the low vapor-density, and by other methods. If phosphorus pentachloride is volatilized in an atmosphere containing an excess either of phosphorus trichloride or of chlorine, the vapor-density as determined by any of the well-known methods is normal. This shows beyond question that an excess of either product of dissociation drives back the dissociation of phosphorus pentachloride. Nothing could demonstrate more conclusively the effect of mass action.

Thermal Changes. — At this stage the study of chemical affinity took an entirely new turn. Up to this time attention had been directed almost exclusively to the material changes which take place in chemical reactions. The nature of the substances before reaction, the velocity and amount of the reaction, and the nature of the products had been studied at length. This is what we would expect, since the transformations of matter are the most obvious results of chemical reactions; and, further, are the most readily studied. There is, however, an entirely different set of changes going on whenever there is chemical action. It was early observed that when we have chemical activity we have thermal changes — heat being either evolved or absorbed, usually evolved. Attention was directed about the middle of the century to a quantitative study of these thermal changes as a means of throwing light on the problem of chemical affinity.

This field was opened up in 1854 by Julius Thomsen,[2] who sought to measure chemical affinity by means of the heat evolved. Thomsen's work is based upon this fundamental proposition, "We can now measure in absolute units the magnitude of the force which is developed in the formation of a compound; it is equal to the amount of heat which is evolved in the formation of the compound." Although we know to-day that this proposition leaves out of account a number of factors, yet it is a very important step in the right direction.

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[1] *Leçons sur la dissociation*, Paris, 1866.

[2] *Pogg. Ann.* **92**, 34 (1854).

A great advance in the application of thermochemical methods to the problem of chemical affinity was made by Berthelot.[1] He began his work in 1867,[2] and during the next fifteen or twenty years, with the coöperation of his students, improved thermochemical methods, and made an enormous number of thermochemical determinations.

As the result of this extended investigation, Berthelot arrived at the following generalization, which has come to be known as the *Third Principle of Thermodynamics*, "Every chemical change which takes place without the aid of external energy, tends to form the substance, or system of substances, which evolves the most heat." Although there are many apparent exceptions to this wide-reaching generalization, yet the number is relatively not as great as we might expect from the unnecessarily severe criticism to which this principle has been subjected. As has been stated, it undoubtedly contains the germ of a great truth.

Williamson's Views on Chemical Equilibrium. — One other investigation must be referred to in this connection, — that of Williamson on the synthesis of ether from alcohol and sulphuric acid. This has already been considered in connection with the origin of the theory of electrolytic dissociation, but its bearing on chemical equilibrium is of epoch-making importance.

Before this time chemical equilibrium was regarded as *static*. When equilibrium was reached, the greater forces overcame the smaller, and the latter were unable to effect any transformation, being completely overpowered by the greater.

Williamson[3] regarded the formation of ether from alcohol and sulphuric acid as taking place in two stages. In the first stage the hydrogen of the sulphuric acid was replaced by the ethyl group. In the second the ethyl in ethyl sulphuric acid was replaced by hydrogen. The reaction in one direction was the reverse of that which took place in the opposite direction, but both reactions were going on simultaneously. If this reciprocal exchange of parts can take place with atoms or groups which are unlike, so much the more can it take place with similar atoms or groups. Between the molecules of any given compound there is, then, a continual interchange of parts taking place; a given atom, which at any moment forms part of one molecule, may the next moment form part of an entirely different molecule. Says Williamson, "In a vessel containing hydrochloric acid, we must not regard the hydrogen atoms as fixedly combined with the chlorine atoms, but any one hydrogen atom may take the place of any other hydrogen atom, being now combined with one chlorine atom and now with another."

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[1] *Essai de Mécanique Chimique.*

[2] *Compt. rend.* **64**, 413.

[3] *Lieb. Ann.* **77**, 37 (1851).

This conception of the condition of things when equilibrium is reached, is fundamentally different from the older or statical view, which regarded the atoms as fixedly combined in molecules. This view of equilibrium, where the atoms are continually changing partners, as it were, we will call the *dynamical view*. Equilibrium is then dynamic, not static, the condition which must be fulfilled being that the same number of transformations must take place in one sense, in a given time, as take place in the opposite sense. We shall see that this lies right at the foundation of our present conception of chemical equilibrium in general.

As has already been mentioned, Clausius[1] proposed a theory similar in kind to that of Williamson, but very different in degree. According to Clausius it is only necessary to assume that a few of the molecules are broken down into parts, which then exchange places with similar parts of other molecules. This is also distinctively a dynamical conception of the condition of equilibrium.

These dynamic conceptions were applied by Pfaundler[2] to dissociation. A vapor dissociates more and more the higher the temperature, due to the fact that more and more molecules are brought into the condition where they break down into their constituents. At the same time a reunion of these constituents is taking place. If the temperature is kept constant at any point, equilibrium will be established; but this equilibrium is dynamic, molecules undergoing decomposition all the while, and other molecules being formed from the decomposition products. The condition of equilibrium is that in a given unit of time the same number of molecules are decomposed as are reformed.

In terms of these dynamic conceptions we can see how mass can have an influence on chemical activity. The larger the number of parts present the more frequently they come in contact, and, consequently, the greater the chemical reaction.

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[1] *Pogg. Ann.* **101**, 338 (1857).

[2] *Ibid.* **131**, 55 (1857).

With this brief historical sketch we shall now turn to a closer study of a generalization which underlies all chemical dynamics and statics, — *The Law of Mass Action.*

THE LAW OF MASS ACTION

The Work of Guldberg and Waage. — Guldberg, who was later professor of applied mathematics at the University of Christiania, and Waage, professor of chemistry at the same institution, were the first to mathematically formulate the effect of mass on chemical activity. Their first preliminary paper was published in Norwegian in 1864. Their epoch-making paper[1] appeared in 1867. In the first part of their paper they review the theories of affinity which had been held. The views of Bergmann and Berthollet are taken up, and it is pointed out that neither is sufficient to account for all the facts known. They attributed this to the lack of a suitable method for determining the magnitude of affinity. They point out that the method of Bergmann, based on the assumption that if the substance B replaces C from a compound with A, giving the compound AB, the affinity between A and B is greater than between B and C, is not satisfactory, since this assumption leaves out of account a large number of conditions which affect the reaction. The attempt to measure the magnitude of chemical affinity by the heat evolved during the reaction was regarded as unsatisfactory, because it depends in part upon the conditions under which the reaction takes place.

Guldberg and Waage point out that in chemistry, as in mechanics, we must study forces by their effects, and the most natural method is to determine forces in the condition of equilibrium; "that is to say, we must study the chemical reactions in which the forces which produce new compounds are held in equilibrium by other forces. This is the case in the chemical reactions where the reaction is not complete but partial, *i.e.* in the reactions where —

"(*a*) Addition and decomposition take place at the same time, and where,

"(*b*) Substitution and reformation proceed simultaneously."

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[1] *Investigations on Chemical Affinities.* University program for the first semester. See also *Ostwald's Klassiker*, No. 104. Edited by R. Abegg.

The authors do not take up in this paper the case of addition and decomposition, or dissociation, since the data available are not sufficient, but develop the law of mass action from a study of the second class of reactions, viz. substitution.

In the development of the law their own words[1] are given: —

"Let us assume that two substances, A and B, are transformed by double substitution into two new substances, A' and B'; and under the same conditions A' and B' can transform themselves into A and B. Neither the formation of A' and B' nor the reformation of A and B are complete, and at the end of the reaction we have the four substances present A, B, A', and B'. The force which causes the formation of A' and B' is in equilibrium with that which causes the formation of A and B. The force which causes the formation of A' and B' increases proportional to the affinity coefficients of the reaction $A + B = A' + B'$, but it depends also on the masses of A and B.

"We have learned from our experiments that, *the force is proportional to the product of the active masses of the two substances A and B.*

"If we designate the active masses of A and B by p and q, and the affinity coefficient by K, the force $= K \,.\, p \,.\, q$.

"As we have often observed, the force Kpq, or the force between A and B, is not the only force which comes into play during the reaction. Other forces tend to retard or accelerate the formation of A' and B'. Let us, however, assume that other forces do not exist, and let us see what formula is developed in this case. We believe that the consideration of this ideal reaction, where only the forces between A and B, and between A' and B' are taken into account, will furnish the reader with a clear and distinct presentation of our theory.

"Let the active masses of A' and B' be p' and q', and the affinity coefficient of the reaction $A' + B' = A + B$ be K'; the force of the reformation of A and B is equal to $K'p'q'$. This force is in equilibrium with the first force, consequently, —

$$Kpq = K'p'q'. \qquad (1)$$

"By determining experimentally the active masses p, q, p', and q', we can find the relation between the affinity coefficients K and K'. On the other hand, if we have found this relation $\frac{K'}{K}$, we can calculate the result of the reaction for any original condition of the four substances."

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[1] *Ostwald's Klassiker*, **104**, 20.

Guldberg and Waage then develop the following relations: —

"If we designate by P, Q, P', and Q', the absolute masses of the four substances A, B, A', and B', before the reaction begins, and let x be the number of atoms of A and B which are transformed into A' and B', and if we let the total volume V during the reaction be constant, we have —

$$p=\frac{P-x}{V},\ q=\frac{Q-x}{V},\ p'=\frac{P'+x}{V},\ q'=\frac{Q'+x}{V}.$$

"By inserting these values into equation (1) and multiplying by V^2, we have —

$$(P-x)(Q-x)=\frac{K'}{K}(P'+x)(Q'+x). \tag{2}$$

"By the aid of this equation the value of x can be easily determined.

"If the two substances A and A' preserve a constant active mass during the reaction, and both have equal value, formula (2) becomes,

$$Q-x=\frac{K'}{K}(Q'+x). \tag{3}$$

"From which,

$$x=\frac{Q-\frac{K'}{K}Q'}{1+\frac{K'}{K}}. \tag{4}$$

"This case is approximately realized if A and A' are solids, while B and B' are liquids."

Guldberg and Waage tested their law by letting A represent barium sulphate, B potassium carbonate, A' barium carbonate, and B' potassium sulphate. They studied this reaction experimentally, using different quantities of barium sulphate and potassium carbonate (giving different values to Q and Q'), and determined the value of x in each case. They then calculated the values of x from their deduction, and showed that the two sets of values agreed very satisfactorily.

Thus originated the law of mass action, which lies at the foundation of chemical dynamics and equilibrium.

Guldberg and Waage point out that these equations hold only for *ideal reactions*, which probably seldom exist. They then consider the other forces which manifest themselves during the reaction. Thus, side reactions take place, giving rise to other products which may either accelerate or retard the original reaction. Again, some of the substances present may be in a different state of aggregation from the remainder — we may have solids as well as liquids entering into the reaction. These and many other influences may come into play, and all of them have to be taken into account in applying the law of mass action to chemical reactions. The remainder of this paper is devoted to a description of experimental data which bear upon the correctness of this law.

In another important contribution[1] in 1879, Guldberg and Waage took up the application of their law to more special cases, such as where one, two, or three of the substances are insoluble, or where one or more of the substances is volatile. Such cases of heterogeneous reactions will be considered in the proper place.

Fundamental Equations of Chemical Dynamics and Equilibrium. — The fundamental conception which underlies the application of the law of mass action to chemical dynamics and equilibrium is that reactions are reversible. A and B react and form A' and B', and at the same time A' and B' react and reform A and B. This is perfectly general. It may, however, happen that one or more of the products is insoluble or gaseous, and escapes from the field of action, which is the same as to say that its active mass is reduced very nearly to zero; but these are special cases where the velocity of the reaction in one direction is very great compared with the velocity in the other direction.

Starting with the fundamental conception of the reversibility of reactions, the velocity of any given reaction as we ordinarily understand it is the difference between the velocity in one direction and the velocity in the other direction. Thus, the velocity with which an ester is formed is really the velocity with which the alcohol and acid combine to form the ester and water, minus the velocity with which the ester and water react to reform the alcohol and acid; in a word, it is the rate at which the amount of ester accumulates.

If we represent the velocity with which the alcohol and acid combine by v, this would, in terms of mass action, be equal to cpq, where p and q are the active masses of the alcohol and acid ($v = cpq$). If we represent the velocity with which water and ester react, forming acid and alcohol, by v_1, in terms of mass action this would be equal to $c_1p_1q_1$, p_1 and q_1 being the active masses of the ester and water. The velocity of the reaction as a whole V, would be the difference between these two velocities, —

$$V = v - v_1 = cpq - c_1p_1q_1.$$

This is the fundamental equation which underlies all chemical dynamics.

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[1] *Journ. prakt. Chem.* N. F. **19**, 69 (1879).

In terms of the principle of reversible reactions the conception of equilibrium becomes very simple. It is but a special case of dynamics, where the two opposite reactions have equal velocities — where $v = v_1$. When this is the case, —

$$cpq = c_1p_1q_1,$$

and this is the fundamental equation of chemical equilibrium.

CHEMICAL DYNAMICS

Velocity of Reactions. — We have seen that the fundamental equation for the velocity of a reaction is, $V = v - v_1 = Cpq - C_1p_1q_1,$ the actual velocity being the difference between the velocities of the two opposite reactions. The study of the velocity of reactions is very much simplified by selecting those which proceed with very great velocity in the one direction, and very slowly in the opposite direction. In such cases the negative member of the above equation disappears, and the velocity which we actually measure is simply the product of the active masses of the substances reacting into the coefficient C.

Monomolecular, or First Order Reactions. — A reaction in which only one substance undergoes change in concentration (which is the same as to say whose active mass changes) is termed a *monomolecular* reaction. If A is the original amount of such a substance present, and if x of it is transformed in time t, the velocity of transformation is, from the law of mass action, —

$$\frac{dx}{dt} = C(A - x),$$

dx is the small amount transformed in the small interval of time dt; C, the velocity coefficient, is a constant. Integrating, we have —

$$-\ln(A - x) = Ct + \text{const.}$$

At the beginning of the reaction $t = 0$, $x = 0$, and we have —

$$-\ln A = \text{const.},$$

$$\ln A - \ln(A - x) = Ct,$$

$$C = \frac{1}{t}\ln\frac{A}{A - x}.$$

Inversion of Cane Sugar. — One of the simplest examples of a reaction of the first order, or a monomolecular reaction, is the inversion of cane sugar by acids. When an aqueous solution of cane sugar is treated with an acid, it breaks down in the sense of the following equation: —

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6},$$

a molecule of cane sugar taking up a molecule of water and breaking down into a molecule of glucose and a molecule of fructose. The cane sugar is the only substance which changes concentration to an appreciable extent, since the water which is used up in the reaction is so small as compared with the total water present as solvent that it can be neglected.

This reaction is unusually simple to study since cane sugar rotates the plane of polarization to the right, while the products of inversion rotate the plane of polarization to the left. By measuring the amount of rotation by means of a polarimeter, we can tell at any moment how much of the sugar has been inverted without interfering with the reaction. Determining x in this manner, observing t, and knowing A the amount of sugar with which we started, we substitute these values in $\frac{1}{t}\ln\frac{A}{A-x} = \text{const.}$, and see whether a constant is obtained, as t, and, consequently, x, vary. The following are a few of the results which were obtained: —

t in Minutes	$\frac{1}{t}\ln\frac{A}{A-x}$	t in Minutes	$\frac{1}{t}\ln\frac{A}{A-x}$
15	0.001360	240	0.001399
45	0.001344	330	0.001465
105	0.001371	510	0.001463
180	0.001378	630	0.001386

In actual practice it is more convenient to use the Briggsian logarithms. This is, of course, 0.4343 times the natural.

It should be mentioned that the above equation for the velocity of inversion of cane sugar was deduced and tested experimentally by Wilhelmy, before the law of mass action was developed. The deduction was based on the assumption that the amount of sugar inverted in unit time is proportional to the amount of unaltered sugar present at that time.

The above equation has been tested for a number of monomolecular reactions, such as the decomposition of arsene into arsenic and hydrogen, the formation of hydrochloric acid and oxygen from chlorine water, the reduction of potassium permanganate by a large excess of oxalic acid,[1] etc.

Catalysis. — In order that the inversion of cane sugar should take place with any considerable velocity, it is necessary that an acid should be present, yet the acid does not enter as such into the reaction. Such reactions are known as *catalytic*, and the substance whose presence is necessary to effect the reaction is called the *catalyzer*. The more concentrated the acid the more rapid the inversion, but the velocity is not exactly proportional to the concentration. The strong acids invert much more rapidly than the weak. The presence of a neutral salt increases the velocity of inversion produced by the strong acids, and diminishes[2] the velocity of inversion of the weak acids.

Since the presence of an acid is necessary to produce any appreciable inversion of cane sugar, and since all acids effect the inversion, we would suspect that the catalyzer in this case was a constituent common to all acids, and such is the fact. The hydrogen ions are the catalyzers, and the velocity of inversion is approximately proportional to the concentration of the hydrogen ions present. This is the same as to say that the catalytic action of different acids is proportional to their strengths, since the strength of an acid is proportional to the amount of its dissociation. Experiment has shown that the velocity of inversion is roughly proportional to the strengths of the acids used.

It is not surprising that there is not exact proportionality, since many influences may come into play which affect the catalytic action of the hydrogen ions.[3] We have already seen the influence exerted by a neutral salt, and other molecules and especially ions may exert a marked influence on the catalysis.

Notwithstanding all of these influences, it has been shown by Trevor[4] that the inversion of cane sugar is a very sensitive means of detecting the presence of hydrogen ions.

We can see from the above example what is meant by catalysis. In order that a substance should act as a catalyzer two conditions must be fulfilled. It must not enter into the reaction, and a very small quantity of the catalyzer must be able to transform a disproportionately large quantity of the substance. From this it seems very probable that the action of catalyzers is a surface action, and that all the phenomena of catalysis are very closely connected with surface energy. At present we are not able to analyze the phenomena of catalysis, or to explain in any detail the action of a catalyzer.

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[1] Harcourt and Essen: *Phil. Trans.* 1866, 193.

[2] *Journ. prakt. Chem.* [2], **32**, 32 (1885).

[3] Arrhenius: *Ztschr. phys. Chem.* **4**, 226 (1889).

[4] *Ztschr. phys. Chem.* **10**, 321 (1892).

Other Catalytic Action of Hydrogen Ions. — If an ester such as methyl acetate is mixed with water, the following reaction takes place: —

$$CH_3COOCH_3 + H_2O = CH_3COOH + CH_4O.$$

If there is a large amount of water present, the reaction proceeds practically to the end, nearly all of the ester being decomposed; but the reaction proceeds very slowly in the presence of water alone.

If, however, an acid is added, the velocity of the reaction is increased; and if the acid is strong, the velocity is very greatly accelerated. The velocity of this reaction is determined by removing a measured volume from the solution from time to time, and titrating the acetic acid set free during the reaction.

A large number of such reactions were studied by Ostwald,[1] who showed that $\frac{1}{t} \ln \frac{A}{A-x}$ is a constant. This proves that the reaction is monomolecular, *i.e.* that during the reaction only one substance changes concentration. Therefore, since the hydrogen ions of the acid do not enter into the reaction, and since a comparatively small quantity of ions can effect the decomposition of a large amount of ester, they act catalytically.

Catalytic Action of finely Divided Metals. — A number of interesting experiments have been recently carried out by Bredig, with the coöperation of Von Berneck,[2] Ikeda,[3] and Reinders.[4] These authors have studied the catalytic action of finely divided metals, and have pointed out certain analogies between them and organic ferments.

The metals were obtained in a finely divided state in water by bringing two bars of the metal close together under water and passing an electric current between the bars under the water. (See p. 252.) The metal was torn off in such a fine state of division that the solution appeared to be perfectly homogeneous when examined under a powerful microscope. Such a solution was shown not to be a true solution, since neither the freezing-point nor vapor-tension of the solvent was lowered. This belongs then to the class of solutions known as colloidal.

By this method solutions of platinum, iridium, gold, silver, cadmium, etc., were prepared.

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[1] *Journ. prakt. Chem.* **28**, 449 (1883).

[2] *Ztschr. phys. Chem.* **31**, 258 (1899).

[3] *Ibid.* **37**, 1 (1901).

[4] *Ibid.* **37**, 323 (1901).

Such solutions of the metals act catalytically, effecting a number of reactions similar to those brought about by organic ferments. The authors showed that those reactions are truly catalytic, by demonstrating that they are reactions of the first order. The reaction which they studied in detail was the decomposition of hydrogen dioxide by a colloidal solution of platinum. They studied the velocity of the decomposition and found that $\frac{1}{t} \ln \frac{A}{A-x}$ was a constant, and therefore the reaction was of the first order. It is known that organic ferments act catalytically.

The most striking analogy, however, between the action of these colloidal solutions of the metals and organic ferments is found in their behavior in the presence of certain poisons. It is well known that mere traces of certain substances are sufficient to prevent the action of organic ferments; these ferments are poisoned, as we say.

Bredig and his pupils[1] have shown that the merest trace of certain substances is sufficient to greatly diminish the catalytic action of the platinum, and in some cases to destroy it entirely. Thus, a gram-molecular weight of hydrogen sulphide in ten million litres of water greatly diminishes the action of the colloidal solution of the metal. And the same effect is produced by a gram-molecular weight of hydrocyanic acid in twenty million litres of water, and by a number of other substances in very small quantity.

Bredig and Reinders[2] have made an elaborate study of the action of "poisons" on the colloidal solution of platinum, and have found, in general, that those substances which are most poisonous to the organic enzymes are most "poisonous" to the metal. Some exceptions were, however, pointed out; but no one can examine the results obtained without being impressed by the large number of agreements.

Bredig is, however, careful to point out in his recent pamphlet on this subject, that the analogy which they have discovered is only an analogy. He does not think that there is any identity between the action of the two classes of substances, which are themselves so different. To quote his own words: "All these facts point to an unmistakable analogy between the contact actions in the inorganic world and the actions of ferments in the organic world. As in the case of my colloidal catalyzers, we are dealing with reactions in which enormously developed surfaces are involved, so is it probable that the same condition obtains in the actions of ferments, enzymes, blood corpuscles, and oxidizing and catalyzing organic substances. We see, therefore, that the organism develops its enormous surfaces in the tissues and colloidal ferments not only because it requires osmotic processes, but on account of the very great catalytic activity of such surfaces. If, as Boltzmann says, the war for existence which living matter must wage is a war about free energy, certainly of all the forms of free energy the *free energy of surface* is the most important for the organism.

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[1] *Ztschr. phys. Chem.* **37**, 1 (1901); **38**, 122 (1901).

[2] *Ibid.* **37**, 323 (1901).

"In conclusion, I need scarcely state that I do not maintain that there is any mysterious identity between the metals and the enzymes. But, without exaggerating the overwhelmingly large number of analogies, we are compelled to regard the colloidal solutions of the metals, in many relations at least, *as inorganic models of the organic enzymes.*"

It seems that this work may prove to be very important as throwing some light on the nature of enzyme action. The enzymes are very complex organic substances, while the colloidal solutions of the metals are as simple as any substances known to the chemist. If the latter effect reactions analogous to the former, by studying the reactions with the simple elements the problem is certainly very much simplified.

Other Monomolecular Reactions. — A number of other monomolecular reactions have been studied, but nothing essentially new has been brought out in connection with them. We should mention the work of Van't Hoff[1] on the transformation of the dibromsuccinic acid formed from fumaric acid and bromine by boiling with water, into brommaleïc acid and hydrobromic acid, in the sense of the following equation: —

$$C_4H_4O_4Br_2 = C_4H_3O_4Br + HBr.$$

Also the transformation of monochloracetic acid into glycolic acid and hydrochloric acid: —

$$CH_2Cl \,.\, COOH + H_2O = CH_2OH \,.\, COOH + HCl.$$

Both of these reactions were shown to be monomolecular, the expression $\frac{1}{t} \ln \frac{A}{A-x}$ coming out a satisfactory constant.

Bimolecular, or Second Order Reactions. — The equation developed above holds where only one substance is undergoing change in concentration. It frequently happens, however, that the active mass of more than one substance changes as the reaction proceeds. Where there is a change in concentration of two substances we have a bimolecular reaction, or a reaction of the second order.

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[1] *Études de dynamique Chimique*, pp. 13 and 113. Amsterdam, 1884. German enlarged edition (Cohen), 1896.

Let us represent the active mass of one substance by A, and of the other substance by B, and by x the portion transformed in time t, we would have from the law of mass action: —

$$\frac{dx}{dt} = C(A - x)(B - x).$$

It is more convenient to take the two substances not in equal weights, but in gram-equivalent weights. When such equimolecular quantities are used $A = B$, and the above equation becomes —

$$\frac{dx}{dt} = C(A - x)^2.$$

Integrating, $$\frac{1}{A - x} = Ct + \text{const.}$$

At the beginning $t = 0$ and $x = 0$, and calculating the constant we have, const. $= \frac{1}{A}\cdot$ Substituting this in the above equation, —

$$\frac{1}{A - x} - \frac{1}{A} = C\,t,$$

$$C = \frac{1}{t}\frac{x}{A(A - x)}.$$

The constant is more frequently expressed thus: —

$$CA = \frac{1}{t}\frac{x}{A - x}.$$

Saponification of an Ester. — A simple example of a reaction of the second order is the saponification of an ester by an alkali, or more accurately expressed by the hydroxyl ions of the alkali. The following well-known reaction expresses what takes place chemically: —

$$CH_3COOC_2H_5 + \overset{+}{Na} + \overset{-}{O}H = CH_3\overset{-}{C}OO + \overset{+}{Na} + C_2H_5OH.$$

Since sodium remains in the ionic condition after the reaction, and since any substance which yields hydroxyl ions will effect the reaction, the equation is better expressed thus: —

$$CH_3COOC_2H_5 + \overset{-}{O}H = CH_3\overset{-}{C}OO + C_2H_5OH.$$

This reaction was studied to test the law of mass action first by Warder,[1] and later by Reicher,[2] Van't Hoff,[3] Arrhenius,[4] Ostwald,[5] and Spohr.[6]

Warder determined the amount of ester saponified by determining by titration the amount of base used up by the acid which was set free from the ester. The values obtained for different intervals of time were very nearly constant, as the following results will show: —

t in Minutes	$\frac{1}{t} \cdot \frac{x}{A-x}$
5	0.113
25	0.108
55	0.108
120	0.113

Effect of the Nature of the Ester and of the Base on the Velocity of Saponification. — The effect of the nature of the ester on the velocity of saponification by a given base was studied by Reicher, who found that the more complex the ester the slower it is saponified. He then studied the velocity of saponification of a given ester by different bases, and found that potassium and sodium hydroxides saponify most rapidly; barium, calcium, and strontium hydroxides somewhat slower; while ammonia is scarcely capable of saponifying an ester at all. Ostwald studied the case of ammonia, and found that the ammonium salt formed greatly diminished the velocity of the reaction. The same fact was verified by Arrhenius, who showed also that the velocity of the saponification as effected by strong bases was only slightly changed by the presence of a salt of that base. These facts, as we shall now see, are just what we would expect from the theory of electrolytic dissociation as applied to these phenomena.

Effect of the Dissociation of the Base. — Since the saponification of an ester is due to hydroxyl ions, it follows from the law of mass action that the velocity of saponification would be determined by the number of hydroxyl ions present; that is to say, by the amount of dissociation of the base. This explains why the most strongly dissociated alkalies, such as potassium and sodium hydroxides, saponify an ester with the greatest velocity. If the base is not completely dissociated, as is always the case except in very dilute solutions, the amount of the dissociation must be taken into account in order that the active mass of the base may be known, the active mass of the base being only the dissociated portion. If we represent the percentage of dissociation of the base by α, this factor must be introduced into the above equation for a second order reaction, which then becomes—

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[1] *Ber. d. chem. Gesell.* **14**, 1361 (1881). Also *Amer. Chem. Journ.* **3**, 340 (1882).

[2] *Lieb. Ann.* **228**, 257 (1885).

[3] *Études de Dynamique Chimique.*

[4] *Ztschr. phys. Chem.* **1**, 110 (1887).

[5] *Journ. prakt. Chem.* **35**, 112 (1887).

[6] *Ztschr. phys. Chem.* **2**, 194 (1888).

$$\frac{dx}{dt} = C_1 \alpha (A - x)^2.$$

We can now see why the presence of a neutral salt has but little influence on the saponifying power of a strong base, but has such a marked influence on the action of a weak base. If the base is strong, it is dissociated to just about the same extent as its salts. Consequently, when the base forms a salt with the acid of the ester, the salt does not yield any larger number of the common cations than were present originally from the dissociating base. There being no appreciable increase in the number of the ions common to both base and salt, the formation of the salt does not drive back the dissociation of the base and, consequently, does not diminish its action.

If, on the contrary, the base is weak, as in the case of ammonia, it is only slightly dissociated. A salt of ammonia is, however, very strongly dissociated. As the ammonium combines with the acid of the ester, forming an ammonium salt which is strongly dissociated, the number of ammonium ions present increases very rapidly. We know that the presence of an excess of either product of dissociation drives back or diminishes the dissociation of the original substance. The increase in the number of ammonium ions present diminishes the dissociation of the ammonium hydroxide, which yields a common ion, and, consequently, diminishes the velocity with which it will saponify an ester. This agrees with the fact that the velocity of saponification of an ester by ammonia decreases much more rapidly than can be accounted for by the diminution in the quantity of ammonia present. Facts and theory are thus qualitatively in perfect accord.

Arrhenius[1] has, indeed, gone farther, and shown that there is a quantitative agreement. From the saponification constants of potassium hydroxide he has been able to calculate those of ammonia in the presence of given quantities of ammonium salts.

Action of Acids on Acetamide.—Another typical second order reaction is the action of acids on acetamide. This has been studied by Ostwald.[2] The reaction is expressed by the following equation:—

$$CH_3CONH_2 + \overset{-}{Cl} + \overset{+}{H} + H_2O = \overset{+}{N}H_4 + \overset{-}{Cl} + CH_3CO_2H.$$

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[1] *Ztschr. phys. Chem.* **2**, 284 (1888).

[2] *Journ. prakt. Chem.* **27**, 1 (1883).

There are only two substances which undergo change in concentration, — the amide and the hydrogen ions. The water which is used up is so small in comparison with the total amount of water present that it can be neglected. A few results obtained by Ostwald with trichloracetic acid show a good constant for a second order reaction.

t is Time in Minutes	$\frac{1}{t}\cdot\frac{x}{A-x}$
15	0.0088
60	0.0088
120	0.0089
180	0.0090
240	0.0090

Second Order Reactions where the Masses are not Equivalent. — It is not always desirable or even possible to use the masses of the two substances in equivalent quantities. In such cases the equation deduced from the law of mass action is more complex, but can be readily integrated. Thus, if the two substances A and B are not in equivalent quantities, —

$$\frac{dx}{dt} = C(A-x)(B-x).$$

Integrating and making $t=0$ and $x=0$, we have —

$$\ln\frac{B(A-x)}{A(B-x)} = (A-B)Ct. \quad \therefore C = \frac{1}{(A-B)t}\ln\frac{(A-x)B}{(B-x)A}.$$

We would not be justified in concluding that this equation holds because the equation for the two substances in equivalent quantities agrees with the facts. Reicher[1] tested the above equation by studying the reaction between ethyl acetate and sodium hydroxide, using different quantities of the two substances. A few of his results will show how satisfactorily the equation is verified. In the first table a large excess of sodium hydroxide was used; in the second table a smaller excess of the hydroxide, and in the third an excess of ester was employed.

	t = Time in Minutes	Constant
I.	374	0.0347
	628	0.0348
	1359	0.0344
II.	393	0.0335
	669	0.0342
	1265	0.0346
III.	342	0.0346
	670	0.0347
	1103	0.0344

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[1] *Lieb. Ann.* **228**, 257 (1885).

A good constant is not only obtained in every series, but we have practically the same constant in all three series, which verifies the above formula in an entirely satisfactory manner.

Trimolecular, or Third Order Reactions. — Just as we may have two substances entering into a reaction, and their active masses consequently changing as the reaction proceeds, so we may have three substances taking part in the reaction. Applying the law of mass action to a third order reaction, we would have —

$$\frac{dx}{dt}=C(A-x)(B-x)(D-x),$$

where A, B, and D represent the masses of the three substances in question.

In such cases it is much simpler to take all three substances in equivalent quantities: $A=B=D$. Then, —

$$\frac{dx}{dt}=C(A-x)^3.$$

Integrating, making $t=0$, $x=0$, we have —

$$C=\frac{1}{t}\,\frac{x(2A-x)}{2A^2(A-x)^2}.$$

If A, B, and D are not taken in equivalent quantities, the equations become very much more complex.[1]

The number of third order reactions known is small, and very few have been studied quantitatively from the standpoint of the law of mass action. A third order reaction in which three substances undergo change in concentration was studied by Noyes and Wason.[2] The reaction is between potassium chlorate, ferrous sulphate and sulphuric acid, and is expressed by the following equation: —

$$6\,FeSO_4 + KClO_3 + 3\,H_2SO_4 = 3\,Fe_2(SO_4)_3 + KCl + 3\,H_2O.$$

This reaction was supposed by Hood,[3] who first studied it, to be a second order reaction, but was shown by Noyes and Wason to be a reaction of the third order. They varied the concentrations of the different substances and determined the value of the constant under very widely different conditions. Although the values found differ as much as 20 per cent, yet they unmistakably verify the above equation for a third order reaction.

Another third order reaction was studied by Noyes,[4] in which only two substances took part. The reaction is between ferric chloride and stannous chloride —

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[1] Fuhrmann: *Ztschr. phys. Chem.* **4**, 89 (1889).

[2] *Ibid.* **22**, 210 (1897).

[3] *Phil. Mag.* [5], **6**, 371 (1878); **8**, 121 (1879); **20**, 323 (1885).

[4] *Ztschr. phys. Chem.* **16**, 546 (1895).

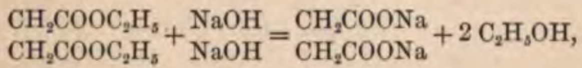
$$2\,FeCl_3 + SnCl_2 = 2\,FeCl_2 + SnCl_4.$$

Although there are only two substances, there are three molecules involved in the reaction, and we would expect it to be a reaction of the third order.

Noyes studied the reaction, using the varying quantities of the two substances, and found fairly satisfactory constants when equivalents were employed, but the values differed very considerably when non-equivalents were used. This might leave some doubt as to whether this is a true reaction of the third order; but in addition to the fact that a fairly satisfactory third order constant was generally obtained, Noyes points out another argument in favor of this being a true third order reaction. If it is a second order reaction, a definite excess of either constituent must produce the same effect; thus, two equivalents of iron on one of tin must have the same influence as two equivalents of tin on one of iron. Noyes found that such is not the case, an excess of ferric chloride accelerating the reaction to a much greater extent than an equivalent of stannous chloride. There can, therefore, be little doubt that this is a true third order reaction.

Reactions which are apparently Trimolecular. — In the last reaction studied only two substances took part, and yet we had to deal with a third order reaction. The difference between this and an ordinary second order reaction between two substances is that two molecules of one substance react with one molecule of the other. We might suspect from this that wherever two molecules of one substance react with one molecule of another substance, we have a third order reaction. Such, however, is not the case.

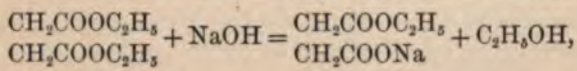
Take the action of a univalent base on the ester of a bivalent acid, — say sodium hydroxide on ethyl succinate, —



$$\begin{matrix}CH_2COOC_2H_5\\CH_2COOC_2H_5\end{matrix} + \begin{matrix}NaOH\\NaOH\end{matrix} = \begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 2\,C_2H_5OH,$$

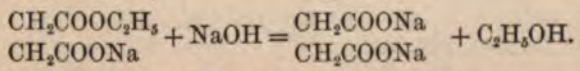
two molecules of the base and one of the ester being involved. Knoblauch[1] has shown that this is not a trimolecular reaction, but is probably made up of the following two bimolecular reactions: —

(1)



$$\begin{matrix}CH_2COOC_2H_5\\CH_2COOC_2H_5\end{matrix} + NaOH = \begin{matrix}CH_2COOC_2H_5\\CH_2COONa\end{matrix} + C_2H_5OH,$$

(2)



$$\begin{matrix}CH_2COOC_2H_5\\CH_2COONa\end{matrix} + NaOH = \begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + C_2H_5OH.$$

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[1] *Ztschr. phys. Chem.* **26**, 96 (1898).

An analogous case, where we might suppose that we were dealing with a trimolecular reaction, is in the saponification of an ester of a univalent acid by means of a bivalent base, — say ethyl acetate by calcium hydroxide, —

$$2\,CH_3COOC_2H_5 + Ca(OH)_2 = (CH_3CO_2)_2Ca + 2\,C_2H_5OH.$$

This has been shown by Reicher[1] to be a bimolecular reaction, just as when sodium or potassium hydroxide is used. The saponification is effected by the free hydroxyl ions, and it does not effect the order of the reaction whether they come from a univalent or a bivalent base.

Reactions of Higher Order. — It is possible to deal with reactions of much higher order in terms of the law of mass action. Thus, a reaction of the nth order would be formulated as follows: —

$$\frac{dx}{dt} = C(A-x)(B-x)(D-x)(E-x)\cdots(n-x).$$

It is, however, not necessary to consider such cases, since there is no reaction known of higher order than the third.

We frequently express chemical reactions as taking place between many more than three molecules, but the study of the velocity of reactions in terms of the law of mass action has taught us that these reactions are not as complex as they seem, being in reality made up of a series of simpler reactions. As an example take the decomposition of arsine by heat. Since the smallest molecule of arsenic known at these temperatures is As_4, we would have to represent the reaction thus: —

$$4\,AsH_3 = As_4 + 6\,H_2,$$

which would make it a fourth order reaction.

The fact is, $\frac{1}{t}\ln\frac{A}{A-x}$ is a constant, which shows that it is a first order reaction. The reaction whose velocity is measured must then be,

$$AsH_3 = As + 3\,H,$$

and subsequently the arsenic atoms must combine and form As_4, and the hydrogen atoms form H_2. Many reactions of a similar character are known, the order being much lower than would be indicated by the usual chemical method of expressing the reaction.

We thus see how the study of the velocity of reactions has thrown light on the inner mechanism of the reactions themselves, and has given us a deeper insight into what actually takes place than could have possibly been obtained by any purely chemical method.

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[1] *Lieb. Ann.* **228**, 257 (1885).

Other Methods of Determining the Order of a Reaction. — The method of determining the order of a reaction thus far considered, consists in measuring the velocity of the reaction and inserting the results into the equations for the constant as obtained from the first, second, and third order reactions. If the values obtained when the experimental results are introduced into the equation for a first order reaction are constant, the reaction belongs to the first order. If a better constant is obtained when the results are introduced into the equation for a second order reaction, the reaction in question belongs to this order, and similarly for a third order reaction.

It, however, frequently happens that none of these equations give a satisfactory constant, and by the above method it would be impossible to determine to which order the reaction belongs. This is due to the fact that in such reactions disturbing influences, such as the setting up of side reactions, or of new reactions between the products of the original reactions, etc., come into play, which affect the velocity coefficients as the reaction proceeds.

Methods for determining the order of a reaction, which largely exclude these influences, have been devised.

The first method we owe to Van't Hoff.[1] The method is based on the effect of change in concentration on the velocity of the reaction, the velocity of a reaction of the nth order being proportional to the nth power of the concentration. The following deduction is given by Van't Hoff, changing the symbols to those used in this volume: —

$$-\frac{dC_I}{dt} = cC_I^n.$$

If we use a different concentration,

$$-\frac{dC_{II}}{dt} = cC_{II}^n.$$

Consequently, $$\frac{dC_I}{dt} : \frac{dC_{II}}{dt} = C_I^n : C_{II}^n;$$

$$n = \frac{\log\left(\frac{dC_I}{dt} : \frac{dC_{II}}{dt}\right)}{\log\,(C_I : C_{II})}.$$

Van't Hoff applied this method of variable volume to the action of bromine on fumaric acid, and also to the polymerization of cyanic acid. The results for the first reaction are as follows: —

The addition of bromine to an aqueous solution of fumaric acid giving rise to dibromsuccinic acid is accompanied by other reactions, which make it impossible to apply directly the equations for a first, second, and third order reaction, and determine the order of the reaction. Van't Hoff applied this method of variable volume or variable concentration in a satisfactory manner. The experiments were carried out by Reicher[1] in Van't Hoff's laboratory.

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[1] *Études de dynamique Chimique*, p. 87.

Time in Minutes	Concentration	$\frac{dC_1}{dt}$
t	C_1	
0	8.88	0.0106
95	7.87	

The value $\frac{dC_1}{dt}$ has been replaced in the calculation by the ratio of the differences $\frac{8.88 - 7.87}{95}$.

Water was then added, increasing the dilution:—

0	C_1	
132	3.81	0.00227
	3.51	

n was then calculated and shown to have the value 1.87. The value found should be 1 for a first order, 2 for a second order, and 3 for a third order reaction. Since disturbing influences must have some effect, we would expect the value found to differ somewhat from these whole numbers. The value 1.87 is sufficiently near to 2 to justify the conclusion that the reaction belongs to the second order.

The *second method* of obtaining the order of a reaction, where disturbing influences come into play, is based upon the principle discovered by Ostwald that for analogous reactions "the amounts of time required to produce a definite degree of decomposition bear constant relations to one another, and are equal to the reciprocals of the corresponding relative affinity coefficients"; in a word, the amounts of time required are inversely as the velocity factors.

This was shown by Ostwald[2] as follows: "The general form of the equation for reaction velocity is,—

$$\frac{dx}{dt} = Cf(x),$$

whose integral is,

$$Ct = \phi(x).$$

"If we let x have the same value in a series of comparable experiments, $\phi(x)$ has a constant value, therefore,—

$$C_1t_1 = C_2t_2 = C_3t_3 \ . \ . \ . \ , \text{ or } C_1 : C_2 : C_3 \ . \ . \ . \ = \frac{1}{t_1} : \frac{1}{t_2} : \frac{1}{t_3} \cdot \ . \ . \ .$$

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[1] *Études de Dynamique Chimique*, p. 89.

[2] *Ztschr. phys. Chem.* **2**, 127 (1888).

"The only assumption made is that the course of the reaction is affected, in all cases, in a like manner by the disturbing influences and side reactions."

Carrying out experiments with different concentrations and allowing the reactions to proceed until equal fractions of the substance are transformed, as Ostwald[1] points out, if the reaction belongs to the first order, the velocity factors and also the amounts of time required are equal; if it is a second order reaction the velocity factors are proportional to the concentrations, and the amounts of time are inversely proportional to the concentrations; if we are dealing with a third order reaction, the velocity factors are proportional to the square of the concentrations, and the amounts of time inversely as the square of the concentrations.

This deduction was applied to experimental results by Noyes,[2] who studied the reaction between hydriodic acid and hydrogen dioxide, also that between hydriodic acid and bromic acid, and several other cases. He found in general that the reactions were of simpler order than would be indicated by the chemical equations expressing them.

Influences which affect the Velocities of Reactions. — The velocities of reactions are considerably affected by a number of influences and conditions, some of which will be considered.

The *influence of temperature* on the velocity of reactions is usually very great. An increase in temperature is generally accompanied by a great increase in the velocity of the reaction, a rise in temperature of 10° frequently doubling, and sometimes tripling the velocity of a reaction. The effect of rise in temperature over a considerable range of temperature is shown by an example given by Van't Hoff.[3] The following reaction with dibromacetic acid was studied: —

$$C_4H_4O_4Br_2 = C_4H_3O_4Br + HBr.$$

The range of temperature was from 15° to 101°, or 86°, and at the higher temperature the velocity was more than three thousand times that at the lower.

The study of the effect of *pressure* on the velocity of reactions has led to interesting results. The pressure of a gas, or the osmotic pressure of a solution, can be readily dealt with from the standpoint of thermodynamics, and the conclusions reached mathematically[1] are, that first order reactions are independent of pressure, second order are proportional to the pressure, while third order are proportional to the square of the pressure.

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[1] *Lehrb. d. Allg. Chem.* II [2], 236.

[2] *Ztschr. phys. Chem.* **18**, 118 (1895); **19**, 599 (1896).

[3] *Vorlesungen über Theoretische und Physikalische Chemie*, I, 223.

The effect of pressure on only a few reactions has been studied experimentally. Rothmund[2] found that the velocity with which cane sugar was inverted by hydrochloric acid was diminished only slightly by changes in pressure. He worked at pressures from one to five hundred atmospheres, and found that at the latter pressure the velocity was about five per cent less than at the former. Röntgen[3] also found that pressure diminished the velocity with which cane sugar is inverted.

Other[4] first order reactions have been studied at different pressures, with the result that increase in pressure slightly increased the velocity of the reaction, but, on the whole, experiment shows that first order reactions are practically independent of pressure.

The *nature of the medium* has a marked influence on the velocity of reactions. This applies especially to the nature of the solvent used. The experimental work of Menschutkin[4] shows the magnitude of this influence. He studied a few reactions in a large number of solvents, and in each case measured their velocities. A few of his results for the action of triethylamine on ethyl iodide, in different solvents, are given. The reaction proceeds as follows: —

$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$

I	II	I	II
Heptane	0.000235	Methyl alcohol	0.0516
Xylene	0.00287	Acetone	0.0608
Benzene	0.00584	α-bromnaphthol	0.1129
Chlorbenzene	0.0231	Acetophenone	0.1294
Ethyl alcohol	0.0366	Benzyl alcohol	0.1330
Allyl alcohol	0.0433		

Column I gives the solvent used; II, the velocity coefficient.

The velocity of the reaction in benzyl alcohol is about seven hundred and forty times that in hexane.

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[1] Van't Hoff: *Vorlesungen über Theoretische und Physikalische Chemie*, I, 235.

[2] *Ztschr. phys. Chem.* **20**, 168 (1896).

[3] *Wied. Ann.* **45**, 98 (1892).

[4] *Ztschr. phys. Chem.* **1**, 611 (1887); **6**, 41 (1890).

We would naturally try to refer the different velocities in the different solvents to the different dissociation powers of the solvents; it is, however, impossible to account for the above facts in this way. The differences between the velocities in the different solvents are very much greater than the differences in the dissociating powers of the same solvents; and, further, the solvents do not always stand in the same order with respect to their dissociating power and the velocity with which a reaction takes place in their presence. Thus, the formation of urea from ammonium cyanate takes place about thirty times as rapidly in ethyl alcohol as in water, and the dissociating power of water is from three to four times[1] as great as that of ethyl alcohol, and other similar examples are known.

A satisfactory explanation of the great differences in the velocities in different solvents has not yet been furnished.

The presence of certain *foreign substances* may considerably affect the velocity of the reaction. Ostwald[2] determined the effect of the presence of neutral salts on the action of hydrochloric and nitric acids on calcium and zinc oxalates. He found that the velocity of the reaction was increased by the presence of the salt, potassium having the greatest influence, ammonium and sodium less, and magnesium still less. On the other hand, Arrhenius[3] found that neutral salts diminished the velocity with which ethyl acetate was saponified by bases, sodium salts having a greater influence than potassium, and barium still greater than sodium. However, results similar to those first considered were obtained by Arrhenius[4] and Spohr[5] from a study of the action of neutral salts on the velocity with which cane sugar is inverted by acids. The neutral salt increased the velocity of the reaction.

Under the head with which we are now dealing attention should be called again to the effect of mere *traces of moisture*[6] on the velocity of many reactions. Dry chlorine is without action on many of the metals, including sodium, as Wanklyn[7] has shown, and Baker[8] and Dixon[9] demonstrated by a number of experiments the comparative inactivity of dry oxygen. That dry hydrochloric acid does not decompose carbonates was shown by Hughes,[1] who also demonstrated that it does not precipitate silver nitrate dissolved in dry ether or benzene. That dry hydrochloric acid gas does not act on dry ammonia gas has been conclusively demonstrated by Baker,[2] and it has even been shown on the lecture table that dry sulphuric acid is without action on dry metallic sodium.[3]

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[1] Jones: *Ztschr. phys. Chem.* **31**, 114 (1900).

[2] *Journ. prakt. Chem.* (N.F.), **23**, 209 (1881).

[3] *Ztschr. phys. Chem.* **1**, 110 (1887).

[4] *Ibid.* **4**, 226 (1889).

[5] *Ibid.* **2**, 194 (1888).

[6] For a fuller discussion of this subject see Jones: *Theory of Electrolytic Dissociation*, pp. 163–170.

[7] *Chem. News*, **20**, 271 (1869).

[8] *Phil. Trans.* 571 (1888).

[9] *Ibid.* 617 (1884).

The presence of moisture is necessary in order that the above-mentioned reactions should take place with any appreciable velocity — moisture is necessary to combination.

On the other hand, a case has been found where moisture effects decomposition. If ammonium chloride is volatilized under ordinary conditions, it is dissociated by heat into ammonia and hydrochloric acid. If, however, the ammonium chloride is carefully dried, it volatilizes without undergoing decomposition, as is shown by the fact that under these conditions its vapor-density is normal. In this case water-vapor seems to be necessary in order that the gases may combine, and is also necessary in order that the compound should be decomposed by heat. That the presence of water is necessary to effect chemical combination is doubtless closely connected with its ionizing power; but it is not a simple matter to explain its action on the vapor of ammonium chloride, causing it to be dissociated by heat.

Two other conditions must be considered in this section, viz. *ignition temperature* and *ignition pressure*. There are many reactions known which take place with an appreciable velocity only above a certain temperature. Below this temperature the reaction apparently does not take place at all. This temperature, at which the reaction apparently begins, is known as the ignition temperature. The study of this temperature for a large number of reactions has been made possible by the recent methods which have been devised for producing low temperatures, especially for producing liquid air on a large scale. It has been found that a large number of reactions, which take place with considerable velocity, do not proceed with any appreciable velocity at these very low temperatures.

A careful study of reactions below the ignition temperature has shown that this is not a point at which the reaction begins, but that there is a very slow reaction below this point; so slow, indeed, that in many cases it cannot be observed at all. In other cases, however, it can be observed, as in the action of phosphorus on oxygen. Below 40°, which is usually taken as the ignition temperature of oxygen and phosphorus, a slow oxidation[1] of the phosphorus takes place, giving rise to the compound P_2O. At the ignition temperature the reaction becomes strongly exothermic, giving the pentoxide of phosphorus. We should, therefore, regard the ignition temperature as that at which any given reaction acquires an appreciable velocity.

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[1] *Phil. Mag.* **34**, 117 (1892).

[2] *Journ. Chem. Soc.* **65**, 611 (1894); **73**, 422 (1898).

[3] *Proceed. Chem. Soc.* 86 (1894).

Just as there is a temperature at which many reactions apparently begin, so there is a pressure at which some reactions between gases and other substances apparently commence to take place. Temperature and pressure, however, act in opposite senses, increase in temperature increasing the velocity of the reaction, while decrease in pressure increases the velocity of the reaction. That pressure at which a reaction begins with an appreciable velocity is known as the ignition pressure, and at lower pressures the reaction proceeds with still greater velocity.

Thus, a mixture of oxygen with phosphene or with silicon hydride explodes on expansion.[2] Aldehyde[3] is not oxidized by oxygen under high pressure, and the ignition temperature of a mixture of hydrogen and oxygen is lowered from 620° to 540° by reducing the pressure from 760 mm. to 360 mm.

Many phenomena similar to the above are known.

Principle of the Coexistence of Reactions. — We have dealt with reactions thus far as if they occur singly, two or more substances reacting giving products which take no part in the reaction. This has been done for the sake of simplicity and clearness, that we might learn how to apply the law of mass action to ideal cases. In fact, most reactions are much more complex, several reactions occurring simultaneously. The question arises how would we apply the law of mass action to these more complex cases? This becomes a simple matter after we are familiar with the fundamental principle that, *every reaction proceeds as if it alone were present.* This applies to a number of coexisting reactions, and is known as the principle of the coexistence of reactions. This has been verified so often by experiment that it is now accepted beyond question.

An application of this principle to a simple catalytic reaction of the first order will serve to make it clear. Take the decomposition of ethyl acetate by water in the presence of acids, and for the sake

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[1] Besson: *Compt. rend.* **124**, 763 (1897).

[2] Friedel and Ladenburg: *Ann. Chim. Phys.* [4], **23**, 430 (1871).

[3] Ewan: *Ztschr. phys. Chem.* **16**, 340 (1895).

of simplicity use acetic acid. Let the amount of acetic ac
represented by A, and the amount of ethyl acetate by B.
velocity of the reaction would be —

$$\frac{dx}{dt} = CA\,(B - x).$$

During the reaction, however, a certain amount x of acetic
set free, and this also acts catalytically on the ester increasi
velocity of the reaction. The velocity due to the acetic ac
free is —

$$\frac{dx}{dt} = Cx\,(B - x).$$

From the principle of the coexistence of reactions the true
ity of the reaction is the sum of these separate velocities, —

$$\frac{dx}{dt} = C\,(A + x)\,(B - x).$$

Integrating,

$$\ln\frac{B(A+x)}{A(B-x)} = C(A + B)t.$$

If the acid used as the catalyzer is different from the acid
ester, the constants are of course different, and we would ha
the sum of the two velocities, —

$$\frac{dx}{dt} = (C'A + Cx)\,(B - x),$$

whose integral is,

$$\ln\left(\frac{B}{B-x}\cdot\frac{C'A+Cx}{C'A}\right) = (C'A + CB)\,t.$$

Cases similar to the above were tested by Ostwald[1] and sat
tory constants obtained. If we understand the principle o
coexistence of reactions, we can proceed to study cases wh
number of reactions are taking place simultaneously.

Side Reactions. — It frequently happens that the subst
which are brought together react in more than one way, giving
than one set of products. In addition to the principal reactio
have then one or more side reactions with velocities of their
The velocity coefficient which we measure is the sum of the
cients of the several reactions.

The simplest case is where a principal reaction of the first
is accompanied by one side reaction of the same order. Fro

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[1] *Journ. prakt. Chem.* [2], **28**, 449 (1883).

law of mass action and the principle of the coexistence of reactions this case would be formulated thus: —

$$\frac{dx}{dt} = C_1(A - x) + C_2(A - x).$$

Integrating,

$$C_1 + C_2 = \frac{1}{t} \ln \frac{A}{A - x}.$$

The velocity constant of the reaction is the sum of C_1 and C_2. It is possible to determine the separate values of C_1 and C_2 by determining the amounts of the products of each reaction. If we represent the ratio between the amounts of these products by r, $\frac{C_1}{C_2} = r$. From this and $C_1 + C_2 = K$, we can calculate C_1 and C_2.

The application of the principle of coexistence of reactions to a second order reaction is as follows. Given a second order reaction with one side reaction also of the second order, —

$$\begin{aligned}\frac{dx}{dt} &= C_1(A - x)(B - x) + C_2(A - x)(B - x)\\ &= (C_1 + C_2)(A - x)(B - x).\end{aligned}$$

Integrating,

$$C_1 + C_2 = \frac{1}{(A - B)t} \ln \frac{B(A - x)}{A(B - x)}.$$

From this the application of the principle to reactions of higher order and also to reactions where one is of one order and the other of a different order is obvious.

Counter Reactions. — It very frequently happens that substances react and give rise to products which in turn react with one another and reform the original substances. In such cases the velocity measured is the difference between the velocities of the two opposite reactions. From the principle of coexistence and the law of mass action, we would have for a first order reaction, —

$$\frac{dx}{dt} = C_1(A_1 - x) - C_2(A_2 + x). \qquad (1)$$

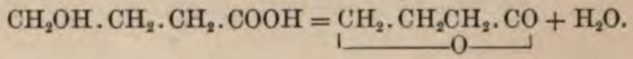
For a second order reaction we would have —

$$\frac{dx}{dt} = C_1(A - x)(B - x) - C_2(C + x)(D + x). \qquad (2)$$

If C and D at the outset were zero, this equation would become —

$$\frac{dx}{dt} = C_1(A - x)(B - x) - C_2 x^2.$$

The equation (1) for the first order reactions was tested by Henry,[1] who studied the dehydration of γ-oxybutyric acid, giving the lactone, —



$$CH_2OH.CH_2.CH_2.COOH = \underbrace{CH_2.CH_2CH_2.CO}_{O} + H_2O.$$

It was also tested by Küster,[2] who studied the transformation of hexachlor-α-keto-β-R-pentane into the α-γ-isomer.

Satisfactory constants were obtained as the result of both investigations.

The equation for a second order reaction was tested by Knoblauch.[3] He studied the reaction between alcohol and acetic acid, and obtained very satisfactory constants.

Since all reactions are to be regarded as reciprocal, every reaction is accompanied by a counter reaction of greater or less magnitude. It, however, frequently happens that the velocity in the one direction is so great and in the other so small that the latter can be disregarded. Where the counter reaction has an appreciable velocity it must be taken into account.

More Complex Reactions. — The conditions which we have just considered are more complex than those which were taken up at first. But there are still more complex cases. We may not only have two or more reactions proceeding in the same or in opposite directions, but we may have the products of a reaction reacting with the products of another reaction, or we may have the products of a reaction reacting with some of the original substances. In such complex cases it is obvious that all the variable quantities must be taken into account.

The detailed study of such cases would scarcely be profitable in this connection, since no new principle is brought out or illustrated. If we understand the application of the law of mass action and the principle of the coexistence of reactions to simpler cases, no serious difficulty should be encountered in applying them to more complex reactions.

Autocatalysis. — We have already seen that certain substances can effect chemical reactions without taking part in them, and are, therefore, said to act by contact or catalytically. Thus, hydrogen ions can cause the inversion of cane sugar in the presence of water. The question which arises is whether a substance may not act catalytically on itself, causing it to enter into reactions. We have already seen one example of the transformation of an oxyacid (γ-oxybutyric) into a lactone with the loss of a molecule of water. This reaction takes place with much greater velocity in the presence of an acid, due to the catalytic action of the hydrogen ions. But these oxyacids, like all other acids, are themselves partly dissociated, yielding, of course, hydrogen ions. If the hydrogen ions from other acids accelerate the velocity of this reaction, why do not the hydrogen ions from this acid itself? This has been tested by adding to this acid one of its neutral salts, which drives back its dissociation. The result is that under these conditions the reaction takes place more slowly, showing that the hydrogen ions from this acid acted catalytically. Such actions have been termed *autocatalytic*.[1]

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[1] *Ztschr. phys. Chem.* **10**, 115 (1892).

[2] *Ibid.* **18**, 161 (1895).

[3] *Ibid.* **22**, 268 (1897).

Heterogeneous Reactions. — The reactions with which we have thus far had to deal are all *homogeneous*, *i.e.* every substance present is in the same state of aggregation before the reaction, and all the products of the reaction are in the same state of aggregation as the original substances. For example, the substances before the reaction are all liquid, and the products all liquid, or the substances are all in solution and the products are all in solution.

We know, however, a large number of chemical reactions where a gas is formed or a solid is formed, and other reactions where a liquid or a solution acts on a solid. In such cases the substances are in different states of aggregation, and such reactions are termed *heterogeneous*. It is obvious that in such cases where there is a surface separating the substances which are in different states of aggregation, the velocity of the reaction will depend upon the magnitude of this surface. This must be taken into account in dealing with the velocity of such reactions. We shall now study a few types of heterogeneous reactions from the standpoint of the law of mass action.

Heterogeneous Reaction of the First Order. — A heterogeneous reaction of the first order is one in which two substances in different states of aggregation react, the active mass of one of them changing as the reaction proceeds, while the active mass of the other, or the surface, remains constant. Applying the law of mass action to such a case, we would have —

$$\frac{dx}{dt} = CS(A - x),$$

where S is the surface exposed to the liquid or solution, A the original concentration of the acid, and x the amount used up.

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[1] Ostwald: *Bericht Sachs. Akad.* (1890), 189.

Integrating, we have —

$$\ln \frac{A}{A-x} = CSt.$$

It will be observed that this equation does not take into account the effect produced by the presence of the compound formed, and in some cases this might be quite considerable.

This equation was tested by Boguski,[1] who studied the action of acids on Carrara marble. Plates of marble of known surface were dipped into acids of different concentrations and kept rapidly in motion, that the surface might not become covered with a layer of the carbon dioxide set free. They were removed, washed, and dried, and the loss in weight determined.

Better constants were, however, obtained by Spring,[2] who studied the action of acids on Iceland spar. He had previously [3] studied the action of acids on marble, but finding this not sufficiently homogeneous, he chose the better crystalline form. The spar was tested not only in its crystal planes, but in two other directions, the one parallel and the other at right angles to the principal axis. Although the velocity of the reaction between the spar and the acid was different in different directions, it was the same in any given direction. The result as a whole was that fairly good constants were obtained; indeed, as good as could be expected under the conditions.

An analogous case, as Ostwald[4] points out, is the solution of solids in liquids, and the separation of solids from supersaturated solutions. Take the first case: The velocity with which the solid dissolves depends upon the magnitude of the surface of contact between the solvent and the solid, and, of course, decreases as the saturation point is reached. We thus see, in terms of chemical dynamics, why it is desirable to have as large a surface as possible of the solid exposed to the liquid. We know in fact that to completely saturate a solution, a large amount of the very finely powdered solid should be added after the saturation point is nearly reached.

If the solution is supersaturated, it can best be brought to the saturation point by adding a large amount of the finely powdered solid, as this reaction also is one where surface comes into play.

Since the velocity with which these processes take place diminishes rapidly as the saturation point is approached, we see why such a long time is required to completely saturate a solution, whether we proceed from the side of the pure solvent or from that of the supersaturated solution.

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[1] *Ber. d. chem. Gesell.* **9**, 1646 (1876); **10**, 34 (1877).

[2] *Ztschr. phys. Chem.* **2**, 13 (1888).

[3] *Ibid.* **1**, 209 (1887).

[4] *Lehrb. d. Allg. Chem.* II, 127, p. 288.

If, during reactions like the above, or like the solution of metals in acids, etc., the surface undergoes appreciable change, this must be taken into account. The way in which this would be done would, of course, depend upon the form of the surface. Since the active mass of a solid depends upon its surface, it is only necessary to know the surface before the reaction began, and the surface after the reaction had taken place, and, consequently, the change in surface, in order to calculate the velocity of the reaction.

Heterogeneous Reaction of the Second Order. — There are many reactions between two homogeneous substances, which give rise to products of a different state of aggregation. The precipitation of one substance by another in inorganic chemistry furnishes examples. Indeed, qualitative and quantitative analyses are based upon this fact. It is, however, difficult, not to say impossible, to measure the velocity with which such reactions take place, because it is so great. That such reactions take place with a finite velocity is quite certain, and it seems probable that methods may be devised for measuring these very great velocities in the future.

A reaction between two solutions giving a solid, with a velocity which can be measured, is the following: —

$$Na_2S_2O_3 + 2\ HCl = 2\ NaCl + H_2O + SO_2 + S.$$

Such a reaction has been studied by Foussereau.[1]

Summary. — After a discussion of the law of mass action as formulated by Guldberg and Waage, it was applied to first order, second order, and third order homogeneous reactions. By means of this law it was shown to be possible to determine the number of molecules which take part in a given reaction, and many of the results obtained pointed to the fact that many of our chemical equations are in error, the apparently complex reactions being made up of several simpler reactions. Two other methods of determining the order of a reaction were taken up, and then some of the influences which affect the velocity of reactions, such as temperature, nature of the medium, foreign substances, traces of moisture, etc. The principle of the coexistence of reactions was then discussed and applied to side reactions and counter reactions. Attention was next turned to heterogeneous reactions of the first and second orders.

With this survey of the field of chemical dynamics we pass to a special phase of reaction velocities, where the two counter reactions have the same velocity, *i.e.* to chemical equilibrium.

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[1] *Ann. Chim. Phys.* [6], **15**, 533 (1888).

CHEMICAL EQUILIBRIUM

Equilibrium in Chemical Reactions. — When substances are brought together which react chemically, the reaction starts with a certain velocity. This becomes less and less as the reaction proceeds, as the active masses of the original substances become less, and the active masses of the products of the reaction become greater. After a time a condition is reached where the products of the reaction attain a maximum value, and do not further increase no matter how long the reaction is allowed to proceed under the given conditions. Since the products of the reaction do not increase beyond this point, the active masses of the original substances do not diminish beyond this point. This condition of a reaction where the quantities of the substances taking part in the reaction do not change, and where the products of the reaction do not change in amount, is known as *the equilibrium of the reaction.*

Let us take an example to illustrate this condition. When ethyl alcohol and acetic acid are brought together, they react, as is well known, in the sense of the following equation: —

$$C_2H_5OH + HOOC.CH_3 = H_2O + CH_3COOC_2H_5.$$

Suppose we use one equivalent of the acid and one equivalent of the alcohol. The reaction starts with a certain definite velocity. This becomes less and less as the reaction proceeds — as the active masses of the alcohol and the acid becomes less and less and the active masses of the products — ethyl acetate and water — become greater and greater. Finally, the masses of the acid and alcohol do not further diminish, but remain constant; and the masses of the ester and water do not further increase. When this relation of things obtains, the reaction has reached the condition of equilibrium.

The Condition of a Reaction when Equilibrium is established. — What is the condition of things in a reaction when equilibrium is reached? Take the above reaction: When equilibrium is reached we have present some free alcohol, some free acid, some of the ester and water. When equilibrium is reached are we to consider the reaction between the alcohol and the acid as having ceased to take place? This was the older way of regarding equilibrium, but it does not accord with the experimental facts. Ethyl alcohol and acetic acid will always react when in the presence of each other, whether or not water or ethyl acetate is present.

It is, however, also a fact that when equilibrium is reached in the above reaction, the amount of the ester formed does not increase. How are these apparently contradictory facts to be explained, and how can we account for the condition of equilibrium?

We have already seen that we must regard chemical reactions in general as reversible; the reaction between the original substances giving rise to certain products, which then react with one another and reform the original substances. In the above reaction the alcohol and acid react forming the ester and water, and then the ester and water react forming the original acid and alcohol. Instead of writing reactions, as we ordinarily do, from left to right, we must write them from left to right and also from right to left. Thus, the above reaction should be written: —

$$C_2H_5OH + HOOC.CH_3 \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

which means that we have two reactions taking place simultaneously in the opposite sense.

This method of regarding reactions not only agrees with the experimental facts, but throws light on the whole problem of the equilibrium of reactions. When, as in the above case, two substances react, they do so with a definite velocity, which becomes less as the reaction proceeds, and the active masses of the original substances become less. As quickly as the products of the reaction (ester and water) begin to be formed, they react with one another with a velocity which at first is very small, since the masses of those substances present are at first very small, but becomes greater and greater as the masses of these substances become greater.

We have, thus, two reactions proceeding in the opposite sense: The one with a velocity which is continually becoming smaller, the other with a velocity which is ever becoming greater. There will be a condition where *these two velocities will become equal, and this is the condition of equilibrium.*

Equilibrium in a chemical reaction is, then, that condition at which the velocities of the two opposite reactions are the same, and this conception greatly simplifies the whole problem. We can apply the law of mass action to the equilibrium of chemical reactions, just as well as to the velocities of such reactions. It is only necessary to make the velocities of the two opposite reactions equal, and we have at once the condition of equilibrium.

We shall now study reactions of different orders in the light of these conceptions.

Equilibrium in First Order Homogeneous Reactions. — We have seen that the velocity of a homogeneous reaction of the first order is expressed by the equation, —

$$\frac{dx}{dt} = C(A - x),$$

where A is the active mass of the original substance, and x the amount transformed during the reaction.

Suppose that the active mass of the substance formed from A is A_1 and that x_1 of this is retransformed into A, the velocity of the second reaction is, —

$$\frac{dx_1}{dt} = C_1(A_1 - x_1).$$

Since the two reactions are exactly the reverse of one another, the one representing the transformation of A into A_1, and the other the transformation of A_1 into A, we have $x = - x_1$ and $dx = - dx_1$. Substituting this value in the last equation, —

$$\frac{dx}{dt} = - C_1(A_1 + x).$$

The velocity of the reaction as a whole being the sum of the velocities of the two individual reactions, —

$$\frac{dX}{dt} = C(A - x) - C_1(A_1 + x).$$

As we have just seen, when equilibrium is established the total velocity of the reaction is zero, consequently, —

$$C(A - x) - C_1(A_1 + x) = 0,$$

or,

$$C(A - x) = C_1(A_1 + x),$$

from which,

$$\frac{C}{C_1} = \frac{A_1 + x}{A - x}.$$

When the equilibrium is established, the amounts of the two substances A and A_1, which are present, are proportional to the velocity constants C and C_1 of the two reactions. This is true independent of the amounts of the substances with which we start; so that knowing the velocity constants of the two reactions we can calculate at once how much of each substance will be present when equilibrium is established.

An example of equilibrium in a homogeneous reaction of the first order would be the transformation of ammonium sulphocyanate, on fusion, into sulphourea. According to Volhard[1] equilibrium is established in this reaction while there is an appreciable quantity of both substances present, and the reaction may readily proceed in either direction, depending upon the amounts of the two substances present. Other examples of equilibrium in first order homogeneous reactions are known, but the number is not large.

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[1] *Journ. prakt. Chem.* **9**, 11 (1874).

Equilibrium in First Order Heterogeneous Reactions. — In such reactions, it will be remembered, the substances are in different states of aggregation: the one a solid and the other a liquid, the one a liquid and the other a gas, or the one a solid and the other a gas, and so on. Since, as we have seen, the active mass of a solid with respect to the other states of aggregation, or of a liquid with respect to a gas is a constant, the active mass of the other substance must also be a constant in order that equilibrium may be established.

The transformation of matter from one state of aggregation into another belongs under this head. The passage from the solid to the liquid state is an example. The solid and liquid are in equilibrium at a definite temperature, regardless of the amount of matter present in either state of aggregation. Similarly, matter in the form of vapor is in equilibrium with the same kind of matter in the form of a liquid, when the amount of vapor in a given volume has reached a certain definite quantity. Such simple transformations as these will be dealt with later by another method, so that no further stress will be laid upon them here.

The reciprocal transformation of cyanogen and paracyanogen is an excellent example of equilibrium in a first order heterogeneous reaction, cyanogen being at ordinary temperatures a gas and paracyanogen a solid. At about 500° cyanogen undergoes transformation into paracyanogen, and above this temperature paracyanogen is transformed into cyanogen, as Troost and Hautefeuille[1] have shown. Equilibrium exists at any given temperature between the two polymeric forms, when the vapor-pressure has reached a certain definite value.

Another example is the well-known reciprocal transformation of yellow and red phosphorus. When yellow phosphorus is heated to 260°, and still better at higher temperatures, it passes over into the red modification, as Hittorf[2] pointed out. When the red modification is volatilized and the vapor suddenly condensed, the yellow modification is obtained again.

These reciprocal transformations have been extensively studied by a number of investigators,[1] and especially by Lemoine, who published his results and the discussion of the whole subject in his book, *Études sur les Équilibres Chimiques,* which is far less known than it deserves to be. For details in this connection reference must be had to his work.

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[1] *Compt. rend.* **66**, 795 (1868).

[2] *Pogg. Ann.* **126**, 193 (1865).

Equilibrium in Second Order Homogeneous Reactions. — The velocity of a reaction in which two substances take part, and where all the substances are in the same state of aggregation, is expressed thus: —

$$\frac{dx}{dt} = C(A-x)(B-x),$$

where A and B are the active masses of the two substances which react.

The velocity of the opposite reaction which takes place between the products of the first reaction is expressed thus: —

$$\frac{dx_1}{dt} = C_1(A_1-x_1)(B_1-x_1).$$

Since we are dealing with equivalent quantities of the different substances, for equilibrium $x = -x_1$ and $dx = -dx_1$.

From the velocities of the two reactions, we have the velocity of the reaction as a whole: —

$$\frac{dX}{dT} = C(A-x)(B-x) - C_1(A_1+x)(B_1+x).$$

For equilibrium $\frac{dx}{dt}$ must be equal to zero, whence, —

$$C(A-x)(B-x) - C_1(A_1+x)(B_1+x) = 0,$$

or,
$$C(A-x)(B-x) = C_1(A_1+x)(B_1+x).$$

$$\because \frac{C}{C_1} = \frac{(A_1+x)(B_1+x)}{(A-x)(B-x)}.$$

If we start with gram-equivalents of A and B, we would represent their active masses by unity. Since at the beginning of the reaction neither A_1 nor B_1 is present, their active masses would be zero. Substituting these values in the above equation, we have —

$$\frac{C}{C_1} = \frac{x^2}{(1-x)^2}.$$

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[1] Troost and Hautefeuille: *Ann. Chim. Phys.* [5], **2**, 145 (1874). Moutier: *Ibid.* [5], **1**, 343 (1874).

The condition of equilibrium in a second order homogeneous reaction is, then, that the velocity coefficients are proportional to the square of the amounts of the substances which have been transformed.

The above equation has been tested by a number of methods. Julius Thomsen employed a method which has already been referred to, but which will be considered more fully in the next chapter, based upon the heat evolved when a salt of one acid is treated with another acid. Knowing the heat evolved when each acid acts separately upon the base, and the heat set free when a salt of one of the acids is treated with the other acid, we have the data necessary for calculating the amount of the base which goes to each acid; in brief, the condition of equilibrium in such a reaction. Without giving details in this connection it may be said that the experimental results are in excellent agreement with the deduction from the law of mass action.

The simplest and most direct method of testing the above equation experimentally was that employed by Ostwald. When substances react chemically there is almost always a change in volume produced, and the change in volume is different for reactions between different substances. Thus, when one acid is neutralized by a given base there results a certain change in volume, which is different from the change in volume produced when another acid is neutralized by the same base. The simplest method of measuring the change in volume is to measure the change in specific gravity, which is proportional to it.

Ostwald carried out the following experiment by the above method. He wished to determine how sulphuric acid and nitric acid will divide a base between them. He determined the specific gravities of normal nitric acid, normal sulphuric acid, and normal sodium hydroxide; also of the solution containing equal volumes of the base and nitric acid, and of the solution containing equal volumes of the base and sulphuric acid. Nitric acid was then added to sodium sulphate, and the specific gravity of the resulting solution determined.

From the above data we could determine at once how the base divided itself between the two acids; how much of the base went to each acid when equilibrium was established. It was found that about one-third went to the sulphuric acid, and about two-thirds to the nitric acid.

Ostwald used his results to test the above deduction by calculating the change in specific gravity which should be produced if this equation is true, and then comparing the values calculated with those found experimentally. The two sets of values agree as satisfactorily as could be expected when we consider that the change in volume which is to be measured is so very small.

Equilibrium in Second Order Heterogeneous Reactions, where One Substance is Solid. — If the reaction is heterogeneous, *i.e.* the substances in different states of aggregation, we may have several possibilities. One substance may be solid and the others liquid, or two or three substances may be solid. We will take up first the simplest case, where one of the products of the reaction is a solid and the other substances are liquid.

We have seen that the active mass of a solid is constant, and we will call this constant S. The velocity of this reaction is —

$$\frac{dx}{dt} = C(A-x)(B-x).$$

The velocity of the opposite reaction is —

$$\frac{dx_1}{dt} = C_1(A_1 - x_1)S.$$

When equilibrium between the two reactions is established we would have —

$$C(A-x)(B-x) = C_1(A_1 + x)S,$$

or,

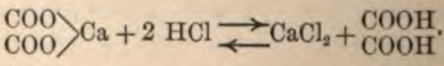
$$\frac{C_1S}{C} = \frac{(A-x)(B-x)}{A_1 + x}.$$

If we start with unit quantities of A and B, at the outset $A_1 = 0$, we would have —

$$\frac{C_1S}{C} = \frac{(1-x)^2}{x}.$$

There are many examples of equilibrium known which belong to this class. Thus, when two soluble substances are brought together and a precipitate is formed and only one soluble substance remains in solution, we have an example of this kind of equilibrium. The action of sulphuric acid on barium chloride, giving barium sulphate and hydrochloric acid, will serve to illustrate this principle.

It is not necessary that the insoluble substance should be formed as the result of the reaction in order that it may belong to this class. One of the substances between which the original reaction takes place may be insoluble. The action of an acid on an insoluble oxalate would be an example. When an equivalent of hydrochloric acid is allowed to act on an equivalent of calcium oxalate, a part of the oxalate dissolves, and we have two reactions taking place in the sense of the following equation: —



$$\begin{matrix}\mathrm{COO}\\ \mathrm{COO}\end{matrix}\!>\!\mathrm{Ca} + 2\ \mathrm{HCl} \rightleftarrows \mathrm{CaCl_2} + \begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix}.$$

When the velocities of the two opposite reactions become equal, equilibrium will be established. The equation of equilibrium for such a case would be —

$$C(A-x)S = C_1(A_1+x)(B_1+x),$$

or,

$$\frac{C_1}{CS} = \frac{A-x}{(A_1+x)(B_1+x)}.$$

If we use unit quantity of acid, at the beginning $A=1$, A_1 and $B_1=0$, the above equation becomes —

$$\frac{C_1}{CS} = \frac{1-x}{x^2}.$$

This reaction has been studied[1] in the way indicated above; also by starting with calcium chloride and oxalic acid, when the equation first deduced applies to it. The conclusions from theory have been verified by experiment.

Equilibrium in Second Order Heterogeneous Reactions, where Two Substances are Solid. — If two of the substances which take part in the reciprocal reactions are solids, their active masses will be constants. The equation for the equilibrium in such cases would be developed as follows. The velocity in the one direction would be —

$$\frac{dx}{dt} = C(A-x)S.$$

In the other direction, —

$$\frac{dx_1}{dt} = C_1(A_1-x_1)S_1.$$

For equilibrium, —

$$C(A-x)S = C_1(A_1+x)S_1,$$

from which —

$$\frac{C_1S_1}{CS} = \frac{A-x}{A_1+x}.$$

This equation was tested experimentally by Guldberg and Waage, and the results published in their *Études sur les Affinités Chimiques.* The following is one of the first examples which they brought forward in support of the law which they had just deduced. They studied the action of potassium carbonate on barium sulphate, which gives rise to potassium sulphate and barium carbonate. The following results are taken from their paper:[2] —

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[1] *Journ. prakt. Chem.* [2] **22**, 251 (1880).

[2] *Klass. d. exakt. Wissenschaft.* **104**, 22. *Journ. prakt. Chem.* [2], **19**, 92 (1879).

A	A_1	x Observed	x Calculated
200	0	39.5	40.0
250	0	50.0	50.0
350	0	71.9	70.0
250	25	30.0	30.0
300	25	40.8	40.0
200	50	0.5 (trace)	0.0

The agreement between the values of x, as found and as calculated, is excellent.

Similar experiments were carried out by Ostwald, using sodium carbonate instead of potassium carbonate. The agreement between the values of x as calculated and as found experimentally is quite satisfactory, but not as close as the results obtained by Guldberg and Waage.

Equilibrium in Second Order Heterogeneous Reactions, where Three Substances are Solid. — If three of the four substances which enter into the two reciprocal reactions are solids, their active masses are all constants. Three of the active masses are constants, and, consequently, the equilibrium depends upon the active mass of the fourth substance, which is not a solid. This case has also been tested experimentally[1] by the action of lead oxide on ammonium chloride, and it was found that the pressure of the ammonia gas set free at any given temperature was independent of the amounts of the solid substances which were present.

The application of the law of mass action to the conditions of equilibrium in chemical reactions has been as successful as to the velocities of these reactions. We can deal with the equilibrium of the more common reactions more simply by means of this law than by any other method which has been thus far proposed. The problem is not only treated by the simplest method available, but by the most exact. The conditions which exist when equilibrium is established are determined with mathematical accuracy, probably far more accurately than by direct experiment. Because of the simplicity and accuracy of the method, it has been employed in connection with the problems of equilibrium in chemical reactions both homogeneous and heterogeneous, and of the first and second orders.

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[1] Isambert: *Compt. rend.* **102**, 1313 (1886).

THE PHASE RULE AND ITS APPLICATION TO CHEMICAL EQUILIBRIUM

The Phase Rule of Willard Gibbs. — The meaning of the Phase Rule can be understood best by studying it in connection with simple substances which exist in different states of aggregation. We know most substances in three different states of aggregation, — solid, liquid, and gas. The different modifications of a substance are known as *phases* of that substance, and we therefore know most substances in three phases. It may occur that the same substance exists in more than three phases, there being two or more phases in the same state of aggregation.

These phases may exist separately, the phase depending chiefly upon the temperature and also to a considerable extent upon the pressure, or they may coexist in a condition of equilibrium with one another. Take a simple substance like benzene; at all ordinary temperatures it exists both in the liquid and vapor phase. At each given temperature the vapor is formed until it acquires a definite pressure, and when this is reached we have an equilibrium between the liquid and vapor phases. If we determine the tension of the vapor of benzene at different temperatures, and then plot the curve expressing the relation between temperature and vapor-pressure, it would have the following form (Fig. 55): —

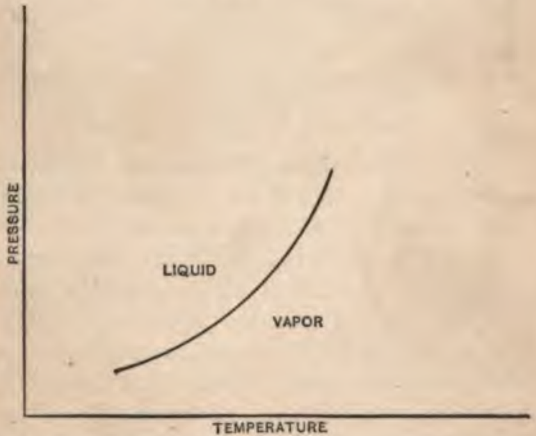

FIG. 55.

The abscissas represent temperatures, and the ordinates pressures. The curve represents conditions of equilibrium between the liquid phase and the vapor phase. Below the curve we have only the vapor, and above only the liquid, in a condition of stable equilibrium.

This is a very simple example, and but serves to show the meaning of the term "phase," and of equilibrium between different phases.

Let us now take a substance which exists in three phases, and a very good example is water. Water exists as a solid, liquid, or gas, depending chiefly upon the temperature, and also upon the pressure. If we draw the temperature-pressure curves representing the conditions of equilibrium between the different phases of water, the curves would take the following forms: —

The curve *PA* (Fig. 56) represents the condition of equilibrium between liquid water and water-vapor. Below this curve the vapor is the stable phase, above it the liquid. The curve *PB* is the line of equilibrium between the liquid and the solid phases of water, the liquid being the stable phase to the right of this curve and above the curve *PA*, while the solid is the stable phase to the left of *PB* and above *PC*. The curve *PC* is the line of equilibrium between the solid phase of water and water-vapor; above this curve and to the left of *PB* ice is the stable condition, while below this curve and *PA* water-vapor is the stable phase.

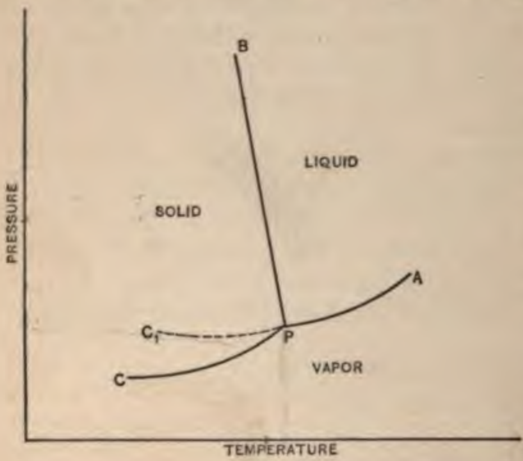

Fig. 56.

It will be observed that the three curves intersect in a point which we have called *P*. This point has properties which make it of special interest. Since it is common to all three curves, it means that at this temperature all three phases of water have exactly the same vapor-pressure. That such is the case can be shown by the following considerations. Take the liquid and solid phases. The point *P* represents the temperature at which ice and water are in equilibrium under their own vapor-tension. Since this is much less than an atmosphere, being in fact about 4 mm., the temperature of the point *P* is slightly above zero, since pressure lowers the freezing-point of water. If the vapor-tension of the ice is not the same as that of the water, it must be either greater or less. If it is greater, the ice will vaporize and the vapor condense as liquid; if it is less, the water will vaporize and the vapor freeze to ice. Since, however, by hypothesis this point represents a condition of equilibrium be tween these phases, where neither can increase at the expense of the other, we could not have either of the above conditions realized. Therefore, since the vapor pressure of the ice cannot be greater than that of the water at this temperature, and cannot be less, it must be equal to it.

A special name has been given to the point P. Since it represents a condition of equilibrium between three phases it is known as a *Triple Point.* The curves PA, PB, and PC represent conditions of equilibrium between two phases, and the areas PAB, PBC, and PCA represent conditions under which only one phase is stable. We can now state and apply the generalization known as the Phase Rule,[1] — *If the number of phases exceeds the number of components by two, the system is non-variant,* or has no degree of freedom. This means that none of the conditions can be varied without destroying the equilibrium. The triple point P is an example of a non-variant system. The number of phases is three and the number of components one, and we cannot vary either the temperature or the pressure without disturbing the equilibrium between the three phases.

If the number of phases exceeds the number of components by one, the system is monovariant, having one degree of freedom. This is the case in the systems PA, PB, and PC. The number of phases is two, and the number of components one, and there exists one variable along these curves. We can vary either the temperature or the pressure, provided we keep on the curve, without destroying the equilibrium between the two phases.

If the number of phases is equal to the number of components, the system is divariant, having two degrees of freedom. This is exemplified by the areas PAB, PBC, and PCA. The number of phases is one, and the number of components one, and two variables exist. We can vary both the temperature and the pressure provided that we keep within the given area without in any wise destroying the equilibrium.

We have now seen what the phase rule is and what is meant by a triple point, a non-variant, monovariant, and divariant system. It is possible to have more than three phases in equilibrium at a point. If there are four, the point is a quadruple point; if five, a quintuple point, and so on. And just as we have had non-variant, monovariant, and divariant systems, so if the number of components is greater than one we may have systems where there are still a larger number of degrees of freedom. With these fundamental conceptions clearly in mind, we shall now apply the phase rule to a number of problems in chemical equilibrium.

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[1] It is a matter of no little pride to Americans to know that this important generalization was discovered by J. Willard Gibbs.

Equilibrium between Different Phases of the Same Substance. — The cases which we have just examined represent conditions of equilibrium between different phases of the same substance. They have, however, been considered only from one standpoint as illustrations of the phase rule. We must now study more carefully a few cases where only one substance is involved.

As an example of *one substance existing in two phases* we may take any two of the phases of water, or the two phases of benzene already considered. The curve represents an equilibrium between the two phases, and since there is one component and two phases, we have a monovariant system. We can vary either the temperature or the pressure, provided we keep within the bounds of this curve, without destroying the equilibrium. The areas above and below the curve represent divariant systems, within which both temperature and pressure can be varied without destroying the phase. Being only one curve there is no point of intersection, and consequently no triple point.

For an example of *one substance existing in three phases* let us return to the temperature-pressure diagram of water. The following contains in addition to the above-mentioned curves the curve PC_1, and this calls for special comment. The three curves PA, PB, PC, in the diagram for water, represent conditions of stable equilibrium; but we know that we may cool water far below its freezing-point without the separation of ice if there is no dust or other solid matter present; and we may heat water more than 100° above its boiling-point without ebullition taking place if all impurities have been removed. These conditions which were not taken into account at all in the original discussion are usually referred to as conditions of unstable equilibrium. Since such conditions simply represent degrees of stability this term has been abandoned in favor of metastable equilibrium.

The curve PC_1 represents a condition of metastable equilibrium for water. The instant a mere fragment of the solid phase, ice, is introduced, freezing begins and ice separates until the metastable passes over into the stable condition. This shows that the stability of the different phases is purely relative.

An idea of the quantity of the phase stable under the conditions, which is required to transform a metastable into a stable phase, can be obtained from an investigation by Ostwald.[1] He has shown that if an almost infinitesimal amount of the stable phase is present, the metastable phase can no longer exist as such, but passes over into the phase which is stable under the conditions.

Attention must be called to one further point in connection with the temperature-pressure diagram of water. The curves do not run out indefinitely from the point P, but stop abruptly in the middle of the diagram. What does this mean?

Take the curve PA, which represents the condition of equilibrium between water and water-vapor. We know that there is a temperature above which the vapor of water cannot be liquefied, the two phases in this region existing as one phase. This is the well-known critical temperature of the substance. At the critical temperature we have also the critical pressure. These two critical constants for water-vapor are represented by the point A as the extreme of the curve PA.

This comparatively simple diagram is, then, a shorthand expression of a large number of experimentally established facts.

We have in sulphur a good example of *one substance existing in four phases.* We know two solid phases of sulphur, — the one stable at ordinary temperatures, crystallizing in the orthorhombic system, the other stable at higher temperatures, crystallizing in the monoclinic system. The orthorhombic melts at 115°, passing over into the liquid phase. If kept at a temperature just below its melting-point, it passes into the monoclinic form. The monoclinic sulphur is also formed when the liquid phase is cooled slowly. Monoclinic sulphur melts higher than orthorhombic, at 120°. When the monoclinic phase is kept at ordinary temperatures, it passes over gradually into the orthorhombic phase, which is the stable form at these temperatures.

At higher temperatures, as we have seen, the orthorhombic passes into the monoclinic. Therefore, at low temperatures, the orthorhombic is the stable, the monoclinic the metastable phase. At higher temperatures, up to 131°, the monoclinic is the stable phase, while the orthorhombic is the metastable phase. The temperature at which the two solid phases are in equilibrium — at which both solid phases can coexist without either passing into the other — is known as the *transition temperature*, and for sulphur this is 95°.6. In addition to the two solid phases of sulphur we have the liquid and the vapor phases.

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[1] *Ztschr. phys. Chem.* **22**, 289 (1897).

If we plot the temperature-pressure diagram of sulphur as we did that of water, it would have the following form: —

The diagram is considerably more complex than the diagram for water, where only three phases were present; yet the principles involved are exactly the same; and if we understood the diagram for water, this should offer no serious difficulty.

Beginning with the conditions of equilibrium between orthorhombic sulphur and sulphur vapor, these are represented by the curve PB. The curve PP_I is the vapor-pressure curve of monoclinic sulphur, while P_IC is the vapor-pressure curve of liquid sulphur. The point P is the transition point of orthorhombic and monoclinic sulphur. The curve PP_{II} represents the conditions of equilibrium between orthorhombic and monoclinic sulphur, and any point on this curve is therefore a transition point. The curve P_IP_{II} represents equilibrium between monoclinic and liquid sulphur, and is therefore the curve of the melting-point of monoclinic sulphur. Just as the curve (PP_{II}) of the transition point of orthorhombic and monoclinic sulphur slopes to the right as it rises, showing an in-

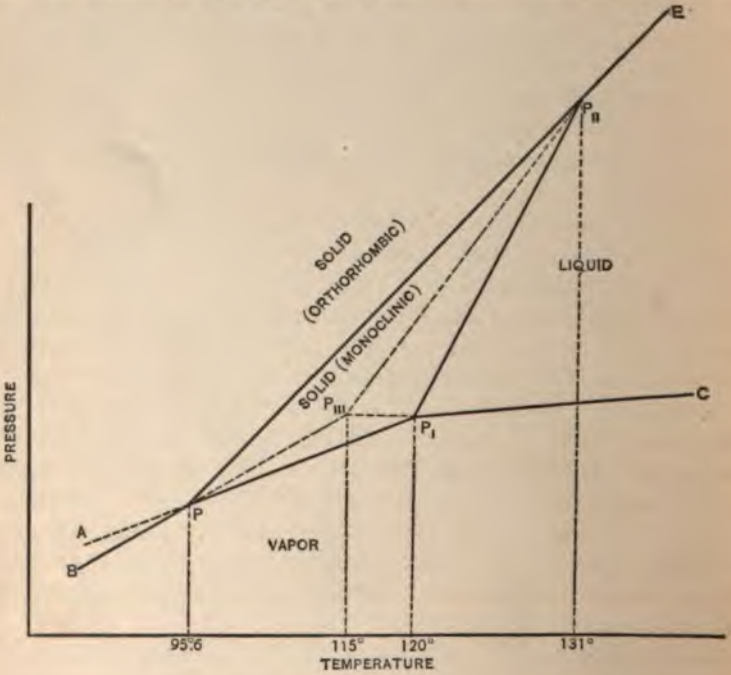

FIG. 57.

crease in temperature with increase in pressure, so the curve of the melting-point of monoclinic sulphur (P_IP_{II}) slopes to the right as it rises. This is but one of many analogies between transition points and melting-points. These two curves, however, meet at the point P_{II}, which corresponds to a temperature of 131°. The curve $P_{II}E$ is the curve of equilibrium between orthorhombic and liquid sulphur, *i.e.* the curve of the melting-point of orthorhombic sulphur with increase in pressure, monoclinic sulphur being incapable of existence beyond 131°, no matter how high the pressure.

Let us turn now to the dotted curves. *PA* represents the vapor-pressure of metastable monoclinic sulphur. This is greater below the transition point, as we would expect, than the vapor-pressure of the stable orthorhombic phase. Above the transition point orthorhombic sulphur is the metastable phase, and it has in this region a higher vapor-pressure than the stable monoclinic phase. This is represented by the curve PP_{III}, the prolongation of *PB*. If now we prolong the curve, P_IC representing equilibrium between liquid sulphur and its vapor until it meets the prolongation of *PB*, it will do so at P_{III}. If now we join P_{III} and P_{II}, the curve will represent the equilibrium between orthorhombic sulphur and liquid sulphur, *i.e.* the melting-point of orthorhombic sulphur, and the effect of pressure as increasing the temperature at which this phase will melt.

We have now examined all the curves in the diagram. Let us see what kinds of systems they represent. The point *P* represents equilibrium between the three phases orthorhombic, monoclinic, and vapor, and is, therefore, a triple point. Similarly, P_I represents equilibrium between monoclinic, vapor, and liquid; P_{II}, between orthorhombic, monoclinic, and liquid, and P_{III} (in the metastable region) between orthorhombic, liquid, and vapor, and these are all triple points. We have, then, four triple points, and since there is one component and three phases the systems are non-variant.

Take the curves. *PB* represents equilibrium between orthorhombic and vapor, PP_I between monoclinic and vapor, P_IC between liquid and vapor, P_IP_{II} between monoclinic and liquid, $P_{II}P$ between orthorhombic and monoclinic.

Take the dotted curves representing equilibria in metastable regions. *PA* is the curve of equilibrium between monoclinic and vapor, PP_{III} between orthorhombic and vapor, P_IP_{III} between liquid and vapor, and $P_{II}P_{III}$ between orthorhombic and liquid.

These systems represent conditions of equilibria between two phases, and since the number of components is one they are monovariant systems.

Take finally the areas. Within BPP_IC sulphur is stable only in the form of vapor, within $CP_IP_{II}E$ the liquid is the stable form, within $EP_{II}PB$ the orthorhombic is the stable phase, and within PP_IP_{II} the monoclinic is the stable form. These areas each represent one stable phase of the substance, and since there is only one component these systems are divariant.

So much for the conditions of equilibria where there is one component and four phases.

We have thus far considered the cases where there is one component and two, three, and four phases, there being two variables, — temperature and pressure. We must now consider a few cases where there is one component and three variables.

Equilibrium between Two Phases of the Same Substance when Three Conditions are Variable. — The phases which we will study are the liquid and vapor phases of a pure substance, like water. The relations between these two phases can be seen by reference to the pressure-volume curves or isothermals, since for each curve the temperature is constant. If we start with a vapor under a small pressure, and increase the pressure, the volume will diminish. The isothermal *ab* (Fig. 58) represents the relations between these two variables. At *b* a portion of the vapor may become liquid; if so, further diminution in volume can take place without increasing the pressure. At *c* all the vapor has become liquid, and beyond this point enormous pressure is required to produce small changes in volume. This is shown by the *dc* portion of the isothermal rising nearly parallel to the ordinate. The isothermals for higher and higher temperatures resemble the one just considered, a greater pressure being required at the higher temperature to liquefy the vapor. Finally the isothermal is reached which passes through the critical point *C*, and this takes the form of the highest curve shown in the figure.

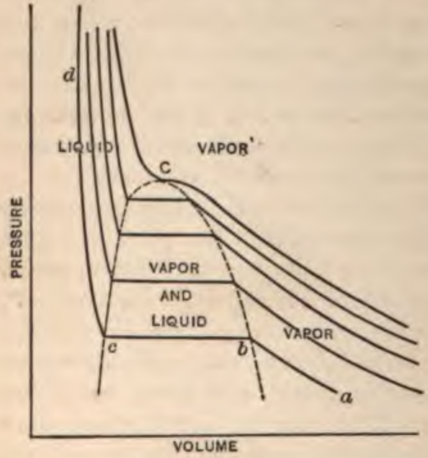

FIG. 58.

In any one of the above curves we have allowed only pressure and volume to vary. Suppose now we allow also temperature to vary, and use the three variables as coördinates on which to plot the relations of the liquid and vapor phases of a substance. The figure would have the form shown in the sketch (Fig. 59). The position of the isothermals is seen at once, also the regions of pure vapor and of pure liquid, and the intermediate heterogeneous region in which both phases are present.

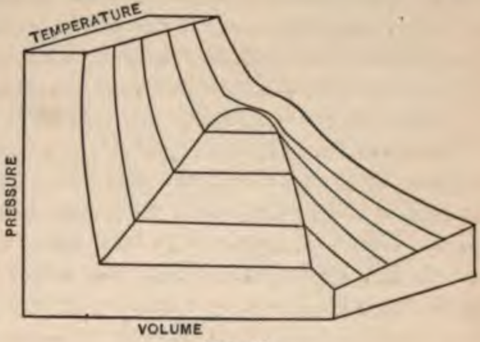

FIG. 59.

We may in the same manner have *equilibrium between three phases of the same substance with three conditions variable*, but a detailed study of such cases would scarcely add to what has already been learned.

Equilibrium between Phases of Two Substances. — We shall not take up the large number of conditions of physical equilibrium between the substances, such as the solubility of a solid in a liquid, etc., since these have been referred to in other connections; but pass at once to the conditions of chemical *equilibrium between two components and three phases.*

A case which is generally discussed because of its comparative simplicity, is the equilibrium between a salt containing water of crystallization and water-vapor. It has been shown that this depends upon the *tension* of the water-vapor, and we must first consider a method by which this is measured.

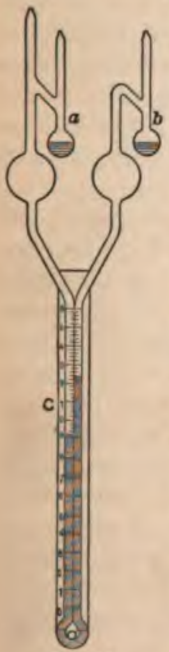

FIG. 60.

The apparatus first used by Frowein[1] was subsequently improved and used by the same investigator.[2] The tensimeter is represented in the following sketch (Fig. 60): — The finely powdered dry salt is placed in the bulb *a*, and sulphuric acid in *b*. The bottom of the bent tube is partly filled with oil, and the apparatus evacuated and sealed. The whole apparatus is placed in a thermostat bath and kept at a constant temperature until there is no further change in the levels of the oil in the two arms. The salt has then exerted its maximum vapor-tension, which is measured by the difference in the heights of the columns of oil in the two arms. If the salt is in the presence of water-vapor at a tension less than the maximum tension of its own water-vapor, it will continue to lose water until this tension is established.

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[1] *Ztschr. phys. Chem.* **1**, 10 (1887). [2] *Ibid.* **17**, 52 (1895).

Take the case of copper sulphate with five molecules of water of crystallization. If this is placed in a desiccator where the tension of the water-vapor is practically zero, it will lose water and pass over into the hydrate with three molecules of water of crystallization. This will continue to lose water and form lower hydrates, and finally the monohydrate. The above transitions can be readily followed, since there is a sudden change in the maximum tension as we pass from one hydrate to another. The tension of aqueous vapor in passing from the pentahydrate to the trihydrate, at the temperature at which the measurements were made (50°), was found to be 47 mm. As soon as the trihydrate was reached the tension of the aqueous vapor fell to 30 mm., and the monohydrate had a vapor-tension of only 4.4 mm. While there is any pentahydrate present the vapor-tension is 47 mm., while any of the trihydrate exists the tension is 30 mm., and so on, the tension being that of the highest hydrate present.

This method has been used to good purpose in discovering the existence of new hydrates, which cannot be prepared by the ordinary methods. The higher hydrates are dehydrated at a constant temperature, and the vapor-pressure measured at short intervals during the process. Sudden drops in the vapor-pressure would show the existence of hydrates containing a definite number of molecules of water.

We are dealing in the above example with equilibrium between three phases and two components; the phases being the higher hydrate, the lower hydrate, and aqueous vapor; the components being the anhydrous salt and water. The number of phases exceeds the number of components by one, and the system is, therefore, monovariant, or has one degree of freedom. We can vary either the temperature or the pressure, but for each temperature there is a definite pressure of the water-vapor.

If we plot these curves in a pressure-temperature diagram, they would have the following form (Fig. 61), the curves *OC*, *OB*, *OA*, corresponding to the penta-, tri-, and mono-hydrates respectively. The vapor-tension curve for ice *OP*, for water *PE*, and for solutions saturated with the pentahydrate P_1D are added. Since a solution has a smaller vapor-pressure than the pure solvent, P_1D falls below PE, and it cuts the curve OP for the vapor-tension of ice at the point P_1, which is the cryohydric point for the solution. This point represents equilibrium between the four phases,—solution, pentahydrate, ice, and vapor,—and is, therefore, a quadruple point.

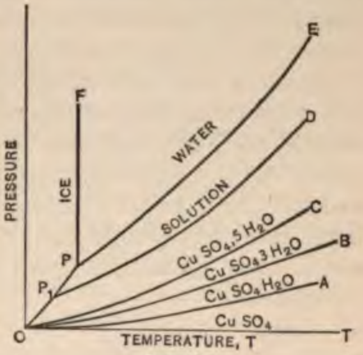

FIG. 61.

If we examine the regions we see that the anhydrous salt can exist in AOT, the monohydrate in AOB, the trihydrate in BOC, the pentahydrate in COP_1D, dilute solutions of the pentahydrate in DP_1PE, water in EPF, and ice in OP_1PF.

Let us turn next to *conditions of equilibrium between two components and four phases.* We shall deal with hydrated salts, *i.e.* those containing a certain number of molecules of water. We may have a number of such hydrates formed by the union of one molecule of the salt with a varying number of molecules of water. The hydrate containing a larger amount of water may pass over, while in solution, into the hydrate with a smaller amount of water if the temperature is raised. Each of these hydrates represents a definite phase, the saturated solution represents another phase, and the water-vapor still another phase.

We shall study in some detail the hydrates formed with ferric chloride, these having been carefully investigated by Roozeboom.[1] He found that there were four hydrates of this substance containing twelve, seven, five, and four molecules of water, and their melting-points were, respectively, 37°, 32°.5, 56°, and 73°.5; at the melting-point the liquid and the solid having the same composition. If to a fused hydrate anhydrous salt is added step by step, a new hydrate will make its appearance containing a smaller number of molecules of water. This is known as the transition temperature. Taking into account the formation of the highest hydrate by adding the anhydrous salt to water, and also the transition temperature from the lowest hydrate to the anhydrous salt, the transition temperatures are: – 55°, 27°,4, 30°, 55°, 66°.

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[1] *Ztschr. phys. Chem.* **10**, 477 (1892).

Roozeboom also determined the composition of the saturated solutions of these hydrates, and from this data, together with the melting-points and transition points, plotted the following curves (Fig. 62),[1] which are given in their original form. The abscissas are temperatures, the ordinates concentration of the solution expressed in number of molecules of Fe_2Cl_6[2] to one hundred molecules of water.

Starting from the point *A*, which represents equilibrium between water and ice, and adding the salt, the freezing-point of water is lowered, and this is represented by the curve *AB*. When the temperature $-55°$ is reached, the solution is saturated with the hydrate $= Fe_2Cl_6 12\,H_2O$,[3] and this separates together with the ice. We have here a cryohydrate, and this is the cryohydric point. If more salt is added, we have then the solubility of the dodecahydrate, and this is represented by the curve *BC*, the point *C* being that at which this hydrate separates in solid form, the saturated solution and the solid having here the same composition. Since the point of solidification is the same as the melting-point, this temperature, 37°, is the melting-point of the dodecahydrate.

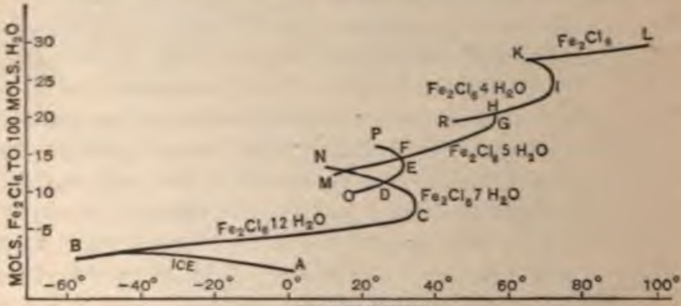

Fig. 62.

If more salt is added to the fused hydrate, the curve takes the form *CDN*, but at the point *D* a new hydrate makes its appearance, containing seven molecules of water. This is, therefore, a transition point. The curve *DN* represents a condition of metastable equilibrium. Starting from *D* and continuing to add the salt, we have the heptahydrate separating at *E* (32°.5). We then pass through the transition point *F* (30°) into the metastable region *FP*. Starting at

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[1] *Ztschr. phys. Chem.* **10**, 502 (1892).

[2] Since Roozeboom uses Fe_2Cl_6 it will be retained.

[3] In connection with these more complex cases symbols are frequently used instead of the names of compounds to simplify comparison with the diagrams.

F and adding more salt, we pass through the melting-point *G* (56°) to the transition point *H* (55°), and so on until *K* is reached, and this is the transition point between the lowest hydrate and the anhydrous salt. The curve *KL* represents the solubility of anhydrous ferric chloride.

This curve presents a number of points of interest. It has a number of quadruple points. The transition points represent equilibria between the two hydrates, the saturated solution, and water-vapor; *i.e.* between four phases, and are therefore quadruple points.

The curves *AB*, *BCD*, *DEF*, *FGH*, *HIK*, and *KL* represent solutions in stable equilibrium with, respectively, ice $Fe_2Cl_6 12 H_2O$, $Fe_2Cl_6 7 H_2O$, $Fe_2Cl_6 5 H_2O$, $Fe_2Cl_6 4 H_2O$, and anhydrous Fe_2Cl_6. The curves *DO*, *DN*, *FP*, *FM*, and *HR* represent equilibria in metastable regions.

As Roozeboom points out, the two branches to each curve (*BCD*, *DEF*, *FGH*, etc.) show that there are two saturated solutions of each hydrate in equilibrium with the hydrate, within certain limits of temperature, the one containing more and the other less water than the solid hydrate. In his own words:[1] "The solubility curves of all the hydrates of ferric chloride present the phenomena that they consist of two branches which coalesce in the melting-point, so that at temperatures below the melting-point two kinds of saturated solutions are possible, the one containing more and the other less water than the solid hydrate.

"I encountered such cases for the first time with hydrated salts in the hexahydrate of calcium chloride.[2] . . . For me the existence of such solutions was only a special case of a general phenomenon." Roozeboom points out that such solutions were to be expected from the thermodynamic deductions of Van der Waals.

One further point must be mentioned. Of the four hydrates of ferric chloride only two were known before Roozeboom carried out his investigation, the one with twelve and the one with five molecules of water, and the composition of the latter was not established with certainty. He found certain peculiarities in his curve, which could not be explained as due to the dodecahydrate nor to the pentahydrate, and was thus led to the discovery of the heptahydrate. In a similar manner the tetrahydrate was discovered.

We see in these facts the real significance of the conception of phases as applied to problems in chemical equilibrium. In this case it has led to the discovery of two new substances, and in other cases to the discovery of a great number of compounds, whose existence could not have been demonstrated by any of the purely chemical methods applicable to such compounds.

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[1] *Ztschr. phys. Chem.* **10**, 486 (1892).

[2] *Ibid.* **4**, 34 (1889).

Equilibrium between Phases of Three Substances. — Systems containing three components are necessarily much more complex than those containing a smaller number. A number of such systems have been studied. Schreinemakers[1] investigated the system consisting of potassium iodide, lead iodide, and water. Meyerhoffer[2] studied cupric chloride, potassium chloride, and water. The system which we shall consider in some detail is potassium sulphate, magnesium sulphate, and water, investigated by Van der Heide.[3]

The system studied by Van der Heide consists of the double sulphate of potassium and magnesium, — schönite, having the composition $K_2Mg(SO_4)_2 . 6 H_2O$, and a newly discovered salt, which, from its analogy to astrakanite, $Na_2Mg(SO_4)_2 . 4 H_2O$, was called potassium astrakanite, having the composition, $K_2Mg(SO_4)_2 . 4 H_2O$. It was found that potassium astrakanite is formed from schönite at 92°, if potassium sulphate is present; it is formed from schönite at 72°, if magnesium sulphate with six molecules of water is present.

Magnesium sulphate with seven molecules of water is transformed, in the presence of schönite, into the sulphate with six molecules at 47°.2. Schönite is formed from the two sulphates at – 3°. The lower limit of investigation is – 4°.5, this being the cryohydric point.

One of the upper limits of investigation is 102°, this being the boiling-point of the solution saturated with potassium astrakanite and potassium sulphate.

The other upper limit of investigation is 103°, being the boiling-point of the solution saturated with potassium astrakanite, and magnesium sulphate with six molecules of water of crystallization.

Van der Heide determined the solubility of *schönite in the presence of potassium sulphate.* The temperatures between which schönite can exist are, – 3°, where schönite breaks down into the separate sulphates, and 92°, where astrakanite is formed. The saturated solution of schönite at 92° gave on analysis, to 100 parts of solution: —

Temp., 92°, K_2SO_4, 17.6, $MgSO_4$, 18.7.

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[1] *Ztschr. phys. Chem.* **9**, 57 (1892). [2] *Ibid.* **5**, 97 (1890); **9**, 641 (1892). [3] *Ibid.* **12**, 416 (1893).

The saturated solution of *potassium astrakanite and potassium sulphate* contained at 98° the following amounts of salt: —

Temp., 98°, K_2SO_4, 18, $MgSO_4$, 18.5.

The composition of the solution *saturated with schönite and magnesium sulphate with seven molecules of water* was also determined. Below −3° schönite undergoes decomposition, the formation of magnesium sulphate with seven molecules of water taking place at 47°.2.

Temp., 22°.0, K_2SO_4, 8.8, $MgSO_4$, 20.1.
Temp., 47°.3, K_2SO_4, 9.9, $MgSO_4$, 27.9.

The composition of the *saturated solution of schönite and magnesium sulphate with six molecules of water* was found to be as follows: It begins at 47°.5 and ends with the formation of astrakanite at 72°,

Temp., 72°, K_2SO_4, 10.7, $MgSO_4$, 29.

Finally, the composition of the *saturated solution of potassium astrakanite and magnesium sulphate with six molecules of water* was ascertained and found to be, —

Temp., 72°, K_2SO_4, 10.8, $MgSO_4$, 29.4.

The above results were plotted in the following diagram (Fig. 63), the abscissas representing temperatures, the ordinates concentrations, above of magnesium sulphate, below of potassium sulphate.

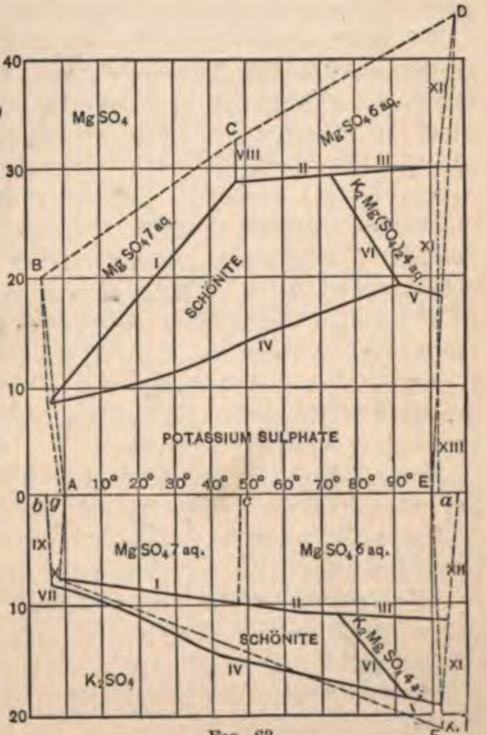

FIG. 63.

Curve I represents the solubility of schönite and magnesium sulphate with seven molecules of water existing between the temperature limits −3° and 47°.2.

Curve II, the solubility of schönite and magnesium sulphate with six molecules of water existing between the temperatures 47°.5 and 72°.

Curve III, the solubility of potassium astrakanite and magnesium sulphate with six molecules of water existing between 72° and 103°.

Curve IV, the solubility of schönite and potassium sulphate between $-3°$ and 92°.

Curve V, the solubility of potassium astrakanite and potassium sulphate existing between 92° and 102°.

Two solubility curves meet at every transition temperature, and from each such temperature we have a third curve, whose direction can be determined from the data already given.

Since the two transition temperatures, 72° and 92°, represent saturation with schönite and potassium astrakanite, the curve joining them (VI) represents saturation with these salts.

Similarly, curve VII, to the left of the point $-3°$, which represents saturation with the two sulphates, K_2SO_4 and $MgSO_4 . 7\,H_2O$, is the curve of saturation of these salts below the transition temperature. It is very short, since it quickly ends in the cryohydric point, $-4°.5$.

Curve VIII represents saturation with the two hydrates of magnesium sulphate, the point *C* corresponding to saturation with magnesium sulphate alone at 48°.2; at this point both hydrates exist together, and the solution is saturated with respect to both.

In addition to the above eight curves we have two starting from the cryohydric point and three in the boiling-point region. These are represented by dotted lines.

Curve IX is the ice line of magnesium sulphate and solution, terminating in the cryohydric point *B* (-6) of magnesium sulphate.

Curve X is the ice line of potassium sulphate and solution, ending in the cryohydric point *G* $(-1°.2)$ of potassium sulphate.

Curve XI is the boiling-point line of solutions saturated with potassium astrakanite. It runs from 102°, the boiling-point of a saturated solution of potassium sulphate, to 103°, the boiling-point of a saturated solution of magnesium sulphate.

Curve XII is the boiling-point line of solutions saturated with magnesium sulphate, ending at *D* (108°), which contains only this salt.

Curve XIII is the boiling-point line of solutions saturated with potassium sulphate, ending at *F* (102°), which contains only this salt.

The data for magnesium sulphate and for potassium sulphate are also represented by dotted lines. The line *BCD* runs from the cryohydric to the boiling-point of magnesium sulphate; the line *GF* from the cryohydric to the boiling-point of potassium sulphate. The lines *BA* and *GA* represent all the freezing-points of solutions of magnesium sulphate and potassium sulphate respectively, meeting in *A*, the freezing-point of water. And, similarly, the lines *DE* and *FE* represent all the boiling-points of solutions of these two sulphates meeting in *E*, the boiling-point of water. Let us now *apply the phase rule to the above system.*

We have three components, $MgSO_4$, K_2SO_4, H_2O, and where there are four phases the system is monovariant. In such a system the solution is always one phase and the vapor another, and along each of the first ten curves we have two other phases represented, thus:—

I. Schönite and magnesium sulphate with 7 H_2O.
II. Schönite and magnesium sulphate with 6 H_2O.
III. Potassium astrakanite and magnesium sulphate with 6 H_2O.
IV. Schönite and potassium sulphate.
V. Potassium astrakanite and potassium sulphate.
VI. Potassium astrakanite and schönite.
VII. Magnesium sulphate + 7 H_2O and potassium sulphate.
VIII. Magnesium sulphate + 7 H_2O and + 6 H_2O.
IX. Magnesium sulphate + 7 H_2O and ice.
X. Potassium sulphate + ice.

At the points where the lines meet, *i.e.* at the transition temperatures, there are five phases, solution, vapor, and as follows:—

$-4°.5$	K_2SO_4, $MgSO_4 \cdot 7\ H_2O$, ice.
$-3°$	K_2SO_4, $MgSO_4 \cdot 7\ H_2O$, schönite.
$47°.2$	$MgSO_4\ 6\ H_2O$, $MgSO_4 \cdot 7\ H_2O$, schönite.
$72°$	$MgSO_4 \cdot 6\ H_2O$, astrakanite, schönite.
$92°$	K_2SO_4, astrakanite, schönite.

The transition points are, therefore, "quintuple points," five phases being in equilibrium at each of these points.

Within each region or area bounded by the curves we have one phase, thus:—

(1) Schönite region, I, II, VI, IV.
(2) Potassium astrakanite region, III, VI, V, XI.
(3) Potassium sulphate region, IV, V, XIII, *FG*, X, VII.
(4) Magnesium sulphate + 7 H_2O, I, VII, IX, *BC*, VIII.
(5) Magnesium sulphate + 6 H_2O, II, III, XII, *DC*, VIII.
(6) Ice, *GAB*, IX, X.

We shall turn now to the next degree of complexity, which is the last case we shall consider.

Equilibrium between Phases of Four Substances. — The case of four components is of special interest, since it includes that large class of chemical reactions known as double decompositions. The case which we shall study in detail is that which was investigated by Löwenherz[1] in Van't Hoff's laboratory. The four substances are potassium chloride, potassium sulphate, magnesium chloride, and magnesium sulphate. These really represent three substances, since the fourth can always be expressed by the other three, thus: —

$$2\ KCl + MgSO_4 = K_2SO_4 + MgCl_2.$$

Therefore, $$K_2SO_4 = 2\ KCl + MgSO_4 - MgCl_2.$$

The fourth substance, water, and the three salts make four components.

Before taking up this case, which is made more complex by the fact that the constituents can combine with one another and form double salts, we shall study a simpler case as Löwenherz did. The example which he selected is, KCl, NaCl, KNO_3, and $NaNO_3$. The graphic representation of any given concentration is as follows (Fig. 64): let the system of four axes meet in *O*, forming the edges of a regular octahedron, *OA*, *OB*, *OC*, and *OD*, two adjoining axes making an angle of 60°, while two opposite axes make an angle of 90°.

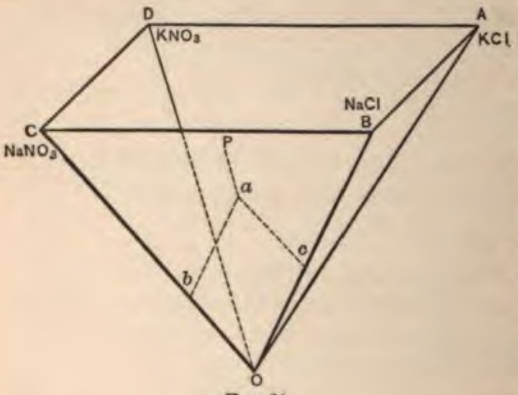

FIG. 64.

If
OA represents the amount of KCl,
OB represents the amount of NaCl,
OC represents the amount of $NaNO_3$,
OD represents the amount of KNO_3,

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[1] *Ztschr. phys. Chem.* **13**, 459 (1894).

the composition at any point *P* is obtained by drawing from *P* a parallel to *DO*, which cuts the plane *OCB* in *A*, and drawing *AC* parallel to *CO*, and *AB* to *BO*,—

aP is the mass of KNO_3,
ac is the mass of $NaNO_3$,
ab is the mass of NaCl.

Since the four salts can exist together only at the transformation temperature, at any other temperature we have the following cases of saturated solutions—solutions saturated with only one, two, and three salts.

If we take first the case where potassium chloride and sodium nitrate can exist together, but not sodium chloride and potassium nitrate, the above three kinds of solutions can be represented by lines and planes (Fig. 65). The solubilities of potassium chloride, sodium chloride, sodium nitrate, and potassium nitrate are represented respectively by *OA*, *OB*, *OC*, and *OD*.

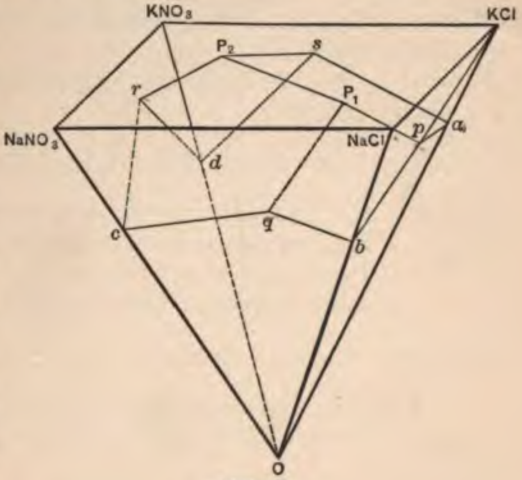

FIG. 65.

In the plane between *oa* and *ob*, we have the line *apb*, *ap* representing the solubility of potassium chloride in the presence of increasing amounts of sodium chloride, and *bp* the solubility of sodium chloride in the presence of increasing amounts of potassium chloride; *p* is the solution saturated with potassium chloride and sodium chloride.

Similar conditions are represented by *bqc*, *crd*, *dsa*. The closed line *apbqcrdsa* represents solutions saturated with one salt, the points *p*, *q*, *r*, *s*, represent solutions saturated with two salts:—

p saturated with KCl and NaCl.
q saturated with NaCl and $NaNO_3$.
r saturated with $NaNO_3$ and KNO_3.
s saturated with KNO_3 and KCl.

There are only two solutions saturated with three salts, since by assumption NaCl and KNO_3 cannot exist together. These are P_1 corresponding to KCl, $NaNO_3$, and NaCl; and P_2 corresponding to KCl, $NaNO_3$, and KNO_3.

P_1 is connected with p by the curve of the solutions saturated with NaCl and KCl.

P_1 is connected with q by the curve of the solutions saturated with NaCl and $NaNO_3$.

P_2 is connected with r by the curve of the solutions saturated with $NaNO_3$ and KNO_3.

P_2 is connected with s by the curve of the solutions saturated with KNO_3 and KCl.

P_1 is connected with P_2 by the curve of the solutions saturated with KCl and $NaNO_3$.

The four planes represent saturated solutions as follows: —

$P_1P_2\,sap$ represents saturation with KCl.
$P_1P_2\,rcq$ represents saturation with $NaNO_3$.
$P_1\,pbq$ represents saturation with NaCl.
$P_2\,rds$ represents saturation with KNO_3.

The figure, therefore, represents the following solutions: —

Unsaturated solutions below $apbqcrdsa\ P_1P_2$.
Supersaturated solutions above $apbqcrdsa\ P_1P_2$.

Saturation with one salt is represented by the four planes just mentioned.

Saturation with two salts is represented by the five lines bounding these planes, also mentioned above.

Saturation with three salts, the two points P_1 and P_2.

Returning now to the case with which we started (KCl, $MgCl_2$, K_2SO_4, $MgSO_4 . 7\,H_2O$), we have in addition to these four salts, schönite formed by the union of the two sulphates, carnallite by the union of the two chlorides, and magnesium sulphate with six molecules of water. The possibilities of combinations of three salts are the following: —

A. schönite, K_2SO_4 and KCl.
B. schönite, $MgSO_4 . 7\,H_2O$ and KCl.
C. $MgSO_4 . 7\,H_2O$, $MgSO_4 . 6\,H_2O$, and KCl.
D. $MgSO_4 . 6\,H_2O$, $KMgCl_3 . 6\,H_2O$, and KCl.
E. $MgSO_4 . 6\,H_2O$, $MgCl_2 . 6\,H_2O$, and $KMgCl_3 . 6\,H_2O$.

The horizontal projection of the results obtained for this system is shown in Fig. 66. The four axes here also are related as the edges of a regular octahedron. These represent the solubilities of the individual salts, — K_2Cl_2,[1] K_2SO_4, $MgSO_4$, and $MgCl_2$. The lines uniting the ends of these areas are really curves, but for our purpose they can be represented as straight.

The line from *J* to *K* represents the solubility of K_2Cl_2 with increasing amount of K_2SO_4, the line *LK* the solubility of K_2SO_4 with increasing amount of KCl; the point *K* where these two lines meet represents the solution saturated at the same time with KCl and K_2SO_4. The line from *L* to *O* represents the solubility of K_2SO_4 with increasing amount of schönite, at *M* the solution saturated with K_2SO_4 and schönite, at *N* the solution saturated with schönite and $MgSO_4 . 7\,H_2O$. The curve from *N* to *O* represents the solubility of $MgSO_4 . 7\,H_2O$, with decreasing amounts of schönite.

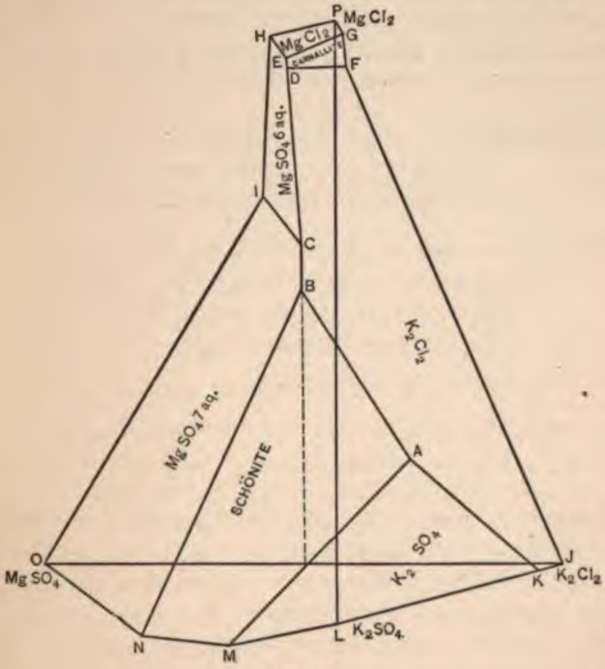

FIG. 66.

The line *OI* represents the solubility of $MgSO_4 . 7\,H_2O$, with increasing amounts of $MgCl_2$, and since the latter combines with some of the water the solution becomes more and more concentrated in $MgSO_4 . 6\,H\,O$ until *I* is reached, when we have saturation with the two compounds $MgSO_4 . 7\,H_2O$ and $MgSO_4 . 6\,H_2O$. From *I* upwards we have saturation with $MgSO_4 . 6\,H_2O$, and an ever increasing amount of $MgCl_2$. At *H* the solution is saturated with respect to $MgCl_2 . 6\,H_2O$ and $MgSO_4 . 6\,H_2O$. *HP* represents the solubility of $MgCl_2 . 6\,H_2O$, with decreasing amount of $MgSO_4 . 6\,H_2O$, and *P* the solubility of the first salt alone. The line *PJ* represents solutions containing $MgCl_2 . 6\,H_2O$, with increasing amounts of K_2Cl_2. At *G* the potassium chloride has become great enough to form carnallite; and from *F* to *J* we have the curve between this salt and potassium chloride.

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[1] K_2Cl_2 is used in order that the unit may refer to corresponding quantities.

The five points in the interior, constructed from the solubility determinations, are *E, D, C, B, A*. They represent solutions saturated with respect to three salts, as follows:—

E. carnallite, $MgSO_4 . 6\,H_2O$, $MgCl_2 . 6\,H_2O$.
D. carnallite, $MgSO_4 . 6\,H_2O$, KCl.
C. $MgSO_4 . 7\,H_2O$, $MgSO_4 . 6\,H_2O$, KCl.
B. $MgSO_4 . 7\,H_2O$, schönite, KCl.
A. K_2SO_4, schönite, KCl.

The seven fields represent the seven salts,—K_2Cl_2, K_2SO_4, schönite, $MgSO_4 . 7\,H_2O$, $MgSO_4 . 6\,H_2O$, $MgCl_2$, and carnallite,—the lines representing the solutions saturated with two salts.

The most important applications of the phase rule to systems containing a number of components have been made in the last few years by Van't Hoff and his pupils. They have studied the conditions of equilibrium between complex systems, in order to obtain some light on the problem of the formation of the great salt beds, and interesting and valuable results have already been obtained. In such connections the phase rule has proved to be of value. It has led to the discovery of many new substances, and the conditions of equilibrium which exist between them.

Before leaving this part of our subject, which has to deal with chemical equilibrium, we must consider one or two matters of more than ordinary importance.

Equilibrium in Condensed Systems.—Van't Hoff[1] has applied the term "condensed system" to those heterogeneous systems where all the components are liquid or solid, there being no gas present.

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[1] *Études de Dynamique Chimique*, pp. 139–148.

These obviously include solids in equilibrium with themselves in the fused condition. This is complete equilibrium, since for any given temperature there is only one pressure under which both phases are stable. The transition point in such a system is, of course, the melting-point of the solid.

Since we are dealing in such systems only with liquids and solids, the effect of pressure on the transformation temperature is very slight, and this is the characteristic of such systems.

Van't Hoff[1] cites as a good example of condensed systems the transformation of cyamelide and cyanuric acid: —

$$\text{Cyamelide} \rightleftarrows \text{cyanuric acid.}$$

The transformation point is about 150°, and cyamelide passes into cyanuric acid by a simple rise in temperature.

Determination of the Transformation Temperature. — *First Method.* Since transformations in condensed systems are always accompanied by volume changes, the specific volumes of the substances before and after the transformation being different, change in volume has been used to determine just when the transformation takes place. As an example, take sulphur; the rhombic modification has a specific volume of $\frac{1}{2.07}$, the monoclinic a specific volume of $\frac{1}{1.96}$.

The apparatus used is known as a dilatometer, consisting of a glass bulb attached to a fine graduated glass tube. The substance whose transformation temperature it is desired to determine is introduced into the bulb, and the remainder of the bulb filled with some indifferent liquid (say an oil), which extends into the graduated tube. The apparatus is then placed in a bath whose temperature can be gradually raised. As the liquid in the dilatometer becomes warmer it expands gradually, the meniscus rising at a regular rate in the graduated tube. When the transformation temperature is reached the transformation takes place, and there is a sudden change in volume which manifests itself by a sudden change in the level of the liquid in the graduated tube.

It has been recommended that a small amount of the products of the transformation be added, in order to insure transformation at the true transformation temperature. Otherwise this temperature might be passed somewhat before the transformation would take place, just as water can be readily supercooled some degrees without the separation of ice. If a small fragment of ice is present, supercooling will be prevented; so, also, if a small particle of the product of the transformation is present, it will prevent the system from passing over into the metastable condition, and will cause the transformation to take place at the true transformation temperature.

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[1] *Études de Dynamique Chimique*, p. 141.

Second Method. Transformations are accompanied not only by volume changes, but also by heat changes. At the transformation temperature heat is either evolved or absorbed, and, by determining when this thermal change occurs, we can determine the transition temperature. The substance in question is placed in a tube, into which a thermometer is introduced. The substance is then warmed or cooled at a fairly uniform rate, and the thermometer noted. When the transformation takes place there is a thermal change, and this is readily seen on the thermometer.

The general rule holds that the system formed at the higher temperature absorbs heat.

Third Method. Another method of determining transformation temperatures is based upon the fact pointed out by Meyerhoffer,[1] that at this temperature the solution of the original substance is identical with that into which it is transformed. The two solutions have the same vapor-tension, solubility, etc. It is only necessary to determine the vapor-tension curves, or the solubility curves of the two substances, and then observe where these become identical, *i.e.* where they cross. This is the transformation temperature.

Fourth Method. Another important method has been devised by Cohen,[2] based upon the concentration element which was studied under electrochemistry. The element used to study transformation temperatures was termed by Cohen the "transformation element." It is simply a concentration element in which the temperatures can be accurately regulated. The following transformation was studied: —

$$ZnSO_4 . 7\,H_2O \rightleftarrows ZnSO_4 . 6\,H_2O + H_2O.$$

The arrangement of the whole apparatus is shown in the sketch (Fig. 67), which includes also the thermostat, *T*. *R* is a rheostat, *S* a key, and *g* the galvanometer.

The vessels *A* and *B* are filled with saturated solutions of $ZnSO_4 . 7\,H_2O$. The solution in *A* is kept for some time above the transformation temperature, when $ZnSO_4 . 7\,H_2O$ passes over into $ZnSO_4 . 6\,H_2O$. The element is then placed in a thermostat at a few degrees below the transformation temperature, and the temperature gradually raised to the transformation point, the galvanometer being read every few minutes. As the temperature approaches that of transformation the readings of the galvanometer become less and less, since the difference between the concentrations on the two sides of the element becomes less and less. At the transformation temperature the concentrations on the two sides become the same, and, consequently, no current flows through the galvanometer.

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[1] *Ztschr. phys. Chem.* 5, 105 (1890).

[2] *Ibid.* 14, 53 (1894).

Since we have a stable phase on one side and a metastable phase on the other, this is known as the "*transformation element with metastable phase.*"

A little later a "*transformation element without metastable phase*" was devised by Cohen and Bredig.[1] This element consists of one electrode surrounded by a normal solution of a salt without the solid phase of the salt; and on the other side a similar electrode surrounded by a saturated solution of the same salt in the presence of the stable solid phase of the salt.

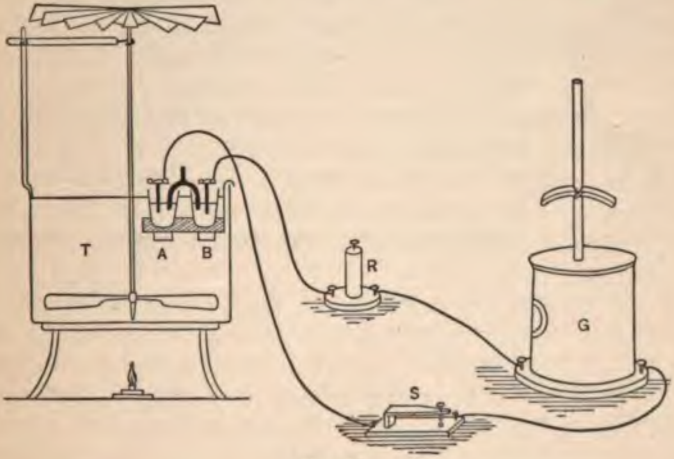

FIG. 67.

The electromotive force of such an element[2] is a function of the solubility of the stable solid phase of the salt. The temperature coefficient of the electromotive force is, therefore, a function of the temperature coefficient of solubility. It is well known that the latter changes suddenly at the transformation temperature, and, therefore, the temperature coefficient of the electromotive force changes suddenly at this temperature.

If we plot the electromotive force of this element as a function of the temperature both above and below the transformation temperature, the point where the two curves cross is the transformation temperature in question.

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[1] *Ztschr. phys. Chem.* **14**, 535 (1894).

[2] *Ibid.* **14**, 536 (1894).

For details in reference to the apparatus used reference must be had to the original paper.

Effect of Temperature on Chemical Equilibrium. — When a system is in equilibrium at one temperature, it does not follow, and it is not generally true, that it is in equilibrium at other temperatures. Sometimes the equilibrium is displaced in the one, and sometimes in the other, direction, the amount of displacement being in some cases very great, in others very small.

A generalization has been reached connecting change in temperature with change in equilibrium, which is very important and accords with what we should think would take place. *The effect of rise in temperature is to favor the formation of that system which absorbs heat when it is formed.* An increase in temperature, therefore, displaces the equilibrium toward the side of that system which is formed with absorption of heat. Examples are very abundant, ordinary vaporization being a striking illustration of the principle, — the higher the temperature the greater the amount of vapor formed.

Effect of Pressure on Chemical Equilibrium. — The action of pressure on chemical equilibrium is through the resulting change in volume. Here also the equilibrium may be displaced in the one or the other direction, or may be only very slightly displaced. A generalization has been reached with respect to the effect of pressure, which is strikingly analogous to that just stated for the effect of temperature.

Increase in pressure diminishes the volume, and therefore favors the formation of that system which occupies the smaller volume. Equilibrium is, then, displaced by increase in pressure toward the system which occupies the less volume.

If there is no change in volume when the transformation of one system into the other takes place, increase of pressure has no influence on the equilibrium. So, also, if the transformation is not accompanied by change in temperature, which is the same as to say that the heat tone of each of the two systems in equilibrium is the same, rise in temperature would have no influence on the equilibrium.

The above two generalizations have been unified by Le Chatelier[1] as follows: —

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[1] *Les Équilibres Chimiques*, p. 210.

"The displacement of a system produced by varying one of the factors of equilibrium is defined by the following law, which I have proposed to call the *law of opposition of action to reaction*.

"*Every change in one of the factors of equilibrium produces a transformation in the system, through which the factor in question is changed in the opposite direction.*"

EQUILIBRIUM IN SOLUTIONS OF ELECTROLYTES

Solubility and Dissociation of Electrolytes. — When different electrolytes are brought in contact with a solvent like water, very different amounts dissolve, depending upon the nature of the substance. The electrolyte passes into solution, until, in a given time, the same amount dissolves as separates from the solution. The solution is then said to be saturated.

In saturated solutions of electrolytes, as in all other concentrated solutions of electrolytes, we have both molecules and ions present. The amount of dissociation depends, as we have seen, upon the nature of the compound. Some electrolytes, such as the weak organic acids and bases, are only slightly dissociated at moderate dilutions, *i.e.* there are only a few ions present and many molecules. Other electrolytes, such as the strong acids and bases, and the salts, are strongly dissociated even in the most concentrated solutions which can be prepared.

The degree of dissociation represents a condition of equilibrium between the molecules and ions present in the solution. When we say that an electrolyte in normal solution is dissociated fifty percent, we mean that when half the molecules are broken down into ions there is equilibrium between the ions and the molecules present.

The condition of equilibrium between molecules and ions, like other conditions of chemical equilibrium, represents not a static but a dynamic condition. This is not a condition where a certain number of molecules have dissociated, and the resulting ions and remaining molecules are in equilibrium; but we must consider the molecules as continually dissociating into ions, and the ions as continually uniting. When equilibrium is reached, the same number of molecules dissociate in a given time as are reformed by combinations of the ions. In a sense, we have here two opposite reactions, the one involving the breaking down of molecules into ions, the other the recombination of the ions to form molecules; and each reaction proceeds with its own definite velocity. When the velocities of the two opposite reactions become equal, equilibri established.

We know already of one condition which can greatly infl this state of equilibrium. The amount of dissociation, *i.e.* the between the number of dissociated and undissociated molecu changed with every change in the dilution of the solution. number of molecules dissociated into ions increases, as we have with increase in the dilution of the solution.

We would naturally ask whether there are any other cond which can affect the amount of the dissociation of electrol There is one which has proved to be of very great importa connection with the whole subject of electrolytic dissociatio this we must study with care before leaving the subject of che equilibrium.

Solubility as affected by an Electrolyte with a Common I We must first ask what effect does the addition of an elect with a common ion have on the solubility of the electrolyte in tion? To make this question clear by an example, what eff the solubility of potassium chlorate would the addition of any ble potassium salt or any soluble chlorate have? Potassium rate dissociates thus: —

$$\mathrm{KClO_3} = \overset{+}{\mathrm{K}} + \mathrm{Cl}\overline{\mathrm{O}}_3;$$

any potassium salt represented by KA would dissociate thus: -

$$\mathrm{KA} = \overset{+}{\mathrm{K}} + \overline{\mathrm{A}};$$

any chlorate represented by $\mathrm{MClO_3}$, thus: —

$$\mathrm{MClO_3} = \overset{+}{\mathrm{M}} + \mathrm{Cl}\overline{\mathrm{O}}_3.$$

The second electrolyte would yield an ion in common with the

This question has been satisfactorily answered by experi If to a saturated solution of potassium chlorate dry potassium ride is added, some of the potassium chlorate is precipitated the solution, showing that its solubility has been diminished b presence of an electrolyte with a common cation. Similar r were obtained when dry sodium chlorate was added to a satu solution of potassium chlorate. Some of the latter salt was pr tated, showing that its solubility was diminished by the prese an electrolyte with a common anion.

Again, prepare a saturated solution of potassium or sodium ride, and pass in dry hydrochloric acid gas. This dissolves yields the common ion, chlorine. The result is that some o potassium or sodium chloride is precipitated from the solution. This fact has long been known, and has been utilized as a means of purifying chlorides, but its relation to other things was entirely concealed. So much by way of *qualitative* demonstration of the principle, that the presence of a compound which yields a common ion diminishes the solubility of the compound in question.

We must now study this phenomenon *quantitatively*, and see what relations exist between the amount of the substance with a common ion which is added, and the amount by which the solubility of the original electrolyte is diminished.

The Deduction of Nernst. — Nernst[1] was the first to solve this question quantitatively from the theoretical standpoint. He applied the law of mass action as follows:[2] If we start with binary electrolytes which are completely dissociated, the product of the active masses must be constant, and equal to the square of the solubility of the salt without the addition of a foreign substance. This he termed m_0, and the solubility of the salt after the addition of the second substance with a common ion m, the amount of the second salt added, in gram molecules per litre, being x: —

$$m(m + x) = m_0^2. \tag{1}$$

The dissociation, however, is not complete in solutions with which we ordinarily have to deal, and this must be taken into account.

Let α_0 be the dissociation of the first substance in saturated solution before the second is added; let α_1 be the dissociation of the added substance and α the dissociation of the first substance in the presence of the second; we must then multiply these factors into the above equation, when it becomes —

$$m\alpha(m\alpha + x\alpha_1) = m_0^2\alpha_0^2. \tag{2}$$

This formula simply expresses the fact that the product of the masses of the ions is constant.

If we turn our attention to the undissociated portion, we find the following relations: Since $m_0\alpha_0$ represents the dissociated portion of the original electrolyte, $m_0(1 - \alpha_0)$ is the undissociated portion; and since $m\alpha$ is the dissociated portion after the second electrolyte is added, the undissociated portion is $m(1 - \alpha)$. The solubility of the undissociated portion is constant, and therefore we have —

$$m_0(1 - \alpha_0) = m(1 - \alpha). \tag{3}$$

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[1] *Ztschr. phys. Chem.* **4**, 372 (1889).

[2] *Ibid.* p. 379.

Solving equations (2) and (3) for m, we have—

$$m = -\frac{x\alpha_1}{2\alpha} + \sqrt{m_0^2\frac{\alpha_0^2}{\alpha_2} + \frac{x^2}{4}\cdot\frac{\alpha_1^2}{\alpha^2}}. \qquad (4)$$

If $\alpha = \alpha_1$, equation (4) becomes—,

$$m = -\frac{x}{2} + \sqrt{m_0^2\frac{\alpha_0^2}{\alpha^2} + \frac{x^2}{4}}.$$

This equation enables us to calculate the solubility in the presence of a second salt with a common ion, from the solubility in pure water the amount of the second salt added, and the amounts of dissociation of the original substance and the added substance.

Nernst tested his equation in a few cases, and found that it held approximately for the solubility of one substance in the presence of another.

Solubility Experiments of Noyes. — The above equation was tested experimentally by Noyes,[1] who applied it to a number of substances. One of the first systems investigated by Noyes was silver bromate with silver nitrate, and with potassium bromate.[2] The following results were obtained:—

AMOUNT $AgNO_3$ OR $KBrO_3$ ADDED TO A SATURATED SOLUTION OF $AgBrO_3$	SOLUBILITY OF $AgBrO_3$ IN THE PRESENCE OF $AgNO_3$	SOLUBILITY OF $AgBrO_3$ IN THE PRESENCE OF $KBrO_3$	SOLUBILITY CALCULATED
0.	0.00810	0.00810	——
0.0085	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

The solubility of silver bromate in the presence of an electrolyte with a common ion agrees very well with that calculated by means of the above equation. It should be observed also that both electrolytes diminish the solubility of the silver bromate to just about the same extent, and that a very small quantity of either produces a great lowering of the solubility.

Other experiments were carried out with thallium salts, which are especially well adapted to this purpose, because they are not very soluble. Thallium nitrate in the presence of potassium nitrate, thallium bromide in the presence of thallium nitrate, and thallium sulphocyanate in the presence of thallium nitrate and of potassium sulphocyanate were studied. The agreement between the solubility of the electrolyte in the presence of the second electrolyte with a common ion, as found and as calculated, is only fairly satisfactory; the solubility as calculated being several per cent less than the value found, and the difference increases as the quantity of the second electrolyte present increases.

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[1] *Ztschr. phys. Chem.* **6**, 241 (1890).

[2] *Ibid.* **6**, 246 (1890).

This discrepancy must be due to one of the following causes: Either the deduction of Nernst is incorrect, or dissociation as calculated from conductivity measurements is not the true value of the dissociation of electrolytes.

The first assumption is scarcely possible since Nernst's deduction is based directly upon the law of mass action, and Noyes concluded that conductivity is not a true measure of dissociation. This conclusion Noyes thought was strengthened by the fact that the Ostwald dilution law does not apply to strongly dissociated electrolytes as measured by the conductivity method.

Noyes investigated the influence of a number of ternary electrolytes, and obtained results similar to those found with binary electrolytes.

Having convinced himself that the conductivity method is not a true measure of dissociation, he reversed the above procedure and used the influence of one salt on the solubility of another with a common ion as a measure of the dissociation of the latter.

Dissociation of Electrolytes as measured by Change in Solubility. — From the above discussion it is obvious that solubility determinations can be used to measure dissociation.[1] Take the two fundamental solubility equations, $(\alpha = \alpha_1)$,

$$m(m+x)\alpha^2 = m_0{}^2\alpha_0^2,$$

and

$$m(1-\alpha) = m_0(1-\alpha_0),$$

and solve them for α, eliminating α_0,

$$\alpha = \frac{m_0 - m}{x}\left(1 + \sqrt{1 + \frac{x}{m}}\right).$$

α is the dissociation of the salt in the presence of the added salt, and is equal to the dissociation of the salt alone in water at the concentration $(m + x)$. From experimental data it is, then, perfectly simple to calculate the dissociation of the salt in question by means of the above equation. This was done by Noyes at first for hydrochloric acid in the presence of thallous chloride, since the latter is only fairly soluble in water, and the above and similar relations hold only for fairly dilute solutions. The results for the dissociation of hydrochloric acid and thallous nitrate, as determined by the solubility method, did not agree with the dissociation of the same substances at the same dilution as determined by the conductivity method. Noyes introduced the dissociation values as found by solubility into the Ostwald equation (dilution law), and obtained a fairly satisfactory constant for a strongly dissociated electrolyte like thallous nitrate. It looked, therefore, as if the Ostwald dilution law would hold also for strongly dissociated electrolytes, when the true values for the dissociation of such substances were ascertained.

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[1] Noyes: *Ztschr. phys. Chem.* **6**, 259 (1890).

A little later[1] Noyes carried out an elaborate investigation along the same line, using thallous chloride as the salt with which to saturate the solution, and then adding one and another of the soluble chlorides, and determining their dissociation. In this calculation it was necessary to know the dissociation of the thallous chloride in order to calculate that of the chloride which was added to its saturated solution, and which precipitated a certain amount of the thallous chloride. Noyes assumed that the dissociation of thallous chloride is the same as that of the alkali chlorides, and, as we shall see, made a slight error which, however, affected all of his calculations. He determined the dissociation of potassium, sodium, and ammonium chlorides by means of the solubility method, and when the values for potassium chloride were introduced into the Ostwald equation, a very good constant was obtained; while the law does not hold at all if the dissociation as measured by conductivity is used.

Noyes also measured the dissociation of a number of ternary chlorides by the solubility method. These included magnesium, calcium, barium, manganous, zinc, cadmium, mercuric, and cupric chlorides. With most of these thallous chloride was used as the less soluble substance with which to saturate the solution, but in some cases lead chloride was employed.

The most important result of this investigation was that the dissociation of electrolytes, as measured by the solubility method, differed from the dissociation of the same solutions of the same substances as measured by the conductivity method. The results of the measurements of dissociation by solubility showed that the Ostwald dilution law applied at least to a large number of strongly dissociated electrolytes, while from the measurements of dissociation by the conductivity method the law did not apply at all to this large and most important class of electrolytes. Taking all of the facts into account, Noyes was led to the conclusion that the conductivity method is not an accurate measure of the dissociation of strongly dissociated electrolytes. It seemed probable, however, that the conductivity method was capable of measuring the dissociation of weakly dissociated compounds with a fair degree of accuracy.

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[1] *Ztschr. phys. Chem.* **9**, 603 (1892).

Thus the problem stood at this time (1892). There were two methods available for measuring electrolytic dissociation,—the conductivity and the solubility method,—and these gave different results. The problem of determining accurately the amount of dissociation was of fundamental importance for the advancement of physical chemistry, and the only two methods available for measuring dissociation gave widely different results. What was to be done in the light of this serious discrepancy?

At the suggestion and under the guidance of Ostwald, Jones[1] improved the freezing-point method of Beckmann until it could be used to measure electrolytic dissociation. He applied it to a number of acids, bases, and salts at dilutions ranging from 0.1 normal to 0.001 normal, and obtained results for the dissociation of these substances which agreed very well with those obtained by the conductivity method. This still did not clear up the problem of measuring dissociation, since we then had two methods of measuring dissociation which gave concordant results, viz. the conductivity method and the freezing-point method, and the solubility method which gave very different results.

Noyes[2] then extended his work with the solubility method in company with Abbot, and found that his original assumption that thallous chloride is dissociated to the same extent as the alkali chlorides, was not correct. He then determined the dissociation of thallous chloride, and when he inserted this value into the equation, and calculated the dissociation of the chloride which had been added to the saturated solution of thallous chloride, the results for the dissociation of the latter agreed satisfactorily with those obtained by the conductivity and freezing-point methods. Thus was the whole problem of measuring electrolytic dissociation cleared up, and to-day we have the three methods,—conductivity, freezing-point, and solubility,—all giving concordant results.

It is a remarkable coincidence that the results originally obtained by Noyes from the solubility method, when inserted into the Ostwald equation gave fairly good constants, and thus indicated that Ostwald's dilution law held also for strongly dissociated electrolytes. Indeed, it was this fact more than any other which confirmed Noyes in the belief that the conductivity method was not a true measure of the dissociation of strongly dissociated substances, and that his solubility method gave the more accurate results. The applicability of the Ostwald dilution law to strongly dissociated electrolytes, we know to-day, was only apparent, subsequent work by all the methods of measuring dissociation showing that it does not hold at all.

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[1] *Ztschr. phys. Chem.* **11**, 110, 529; **12**, 623 (1893).

[2] *Ibid.* **16**, 125 (1895). *Ibid.* **26**, 152 (1898).

When it was found that the three methods mentioned above gave concordant results for the dissociation of electrolytes, it was a matter of great relief to all who were working on this problem, not simply because these fundamental values were placed beyond question, but a great number of relations were thus cleared up. Each method was based upon a different principle; and while there was discordance in the results, there was more or less confusion and doubt in many directions.

Summary of the Discussion of Equilibrium. — The fundamental idea underlying the study of chemical equilibrium is that it is dynamic. Equilibrium in chemical reactions was studied first as a special case of the velocities of reactions, where the velocities of the two opposite reactions are equal. The phase rule was then briefly discussed, and a few of its simpler applications to systems containing one component, two components, three components, and four components. Equilibrium was studied where two conditions are variable, say temperature and pressure, and also when three conditions are variable, say temperature, pressure, and volume, and the corresponding diagrams plotted. Some of the applications of the phase rule, not simply as a system of classification, but as a direct guide in experimental work, were considered. This was seen to be the case especially where the number of components is large, or where the older methods of investigation are insufficient on account of the comparative complexity of the phenomena dealt with. The methods of determining the temperature of transformation were considered, also the effect of temperature and pressure on chemical equilibrium, and then attention was directed to a special case of equilibrium which has proved to yield extremely important results. This refers to the effect of one salt on the solubility of another with a common ion, which has led to an important method of measuring electrolytic dissociation.

CHAPTER X

MEASUREMENTS OF CHEMICAL ACTIVITY

METHODS EMPLOYED AND SOME OF THE RESULTS OBTAINED

Great Differences in the Activities of Substances. — The student of chemistry recognizes at the very outset the great differences between the chemical activities of different substances. Some substances react with the greatest ease, and often with violence, while others do not react at all; and all intermediate stages of activity exist. Take the action of acids on metals. Some acids act on a given metal very readily, others act more slowly, while others scarcely act at all.

A problem which has attracted the attention of chemists from early times is the measurement of the relative activities of substances. When we review the history of chemistry we find "affinity tables," as we have seen, obtained by a number of methods. These are mainly of historical interest to-day, since many of the methods which were used were either not accurate or did not measure the quantities alone with which they were supposed to deal.

The importance of this problem is obvious, since if we knew the relative affinities of all chemical substances, we should be in a position to say just what would take place when such substances were brought into the presence of one another. We believe that at present we have methods of solving this problem in a large number of cases, and such will be considered in this chapter together with some of the more important results which have been obtained.

Principles upon which the Measurement of Chemical Activity is Based. — In the study of chemical dynamics we saw that reactions proceed with very different velocities under conditions which, at first sight, seem comparable. Take the inversion of cane sugar by acids, the velocity of inversion depends greatly upon the nature of the acid used. If we use the same quantities of different acids, the velocities will vary from acid to acid, and may be a hundred times as great for one acid as for another. Take, on the other hand, the saponification of esters by bases; the velocity depends upon the nature of the base used, and varies greatly from one base to another. The velocity with which a reaction proceeds has been used as a measure of the chemical activities of the substances which take part in the reaction. If we are dealing with reactions like the above, and measure the velocities with which a number of acids invert cane sugar, or a number of bases saponify an ester, we have at once the relative activities of the acids, or bases, in question. This is known as *the dynamical method of measuring chemical affinity.*

When we were studying the conditions of chemical equilibrium, we saw that some reactions proceed very far before equilibrium is reached, while in others equilibrium is established when only a small part of the substance has undergone transformation. We recall that equilibrium in a chemical reaction represents that condition where the two opposite reactions have equal velocities. Knowing the conditions which exist when equilibrium has been established, we can calculate the relative activities of the substances which take part in the reactions. This method of measuring chemical activity is known as *the equilibrium or statical method.*

The Dynamical Methods of measuring Chemical Affinity. (A) **Inversion of Cane Sugar.** — We have already seen that acids in the presence of water have the power of causing cane sugar to take up a molecule of water and then breaking down into glucose and fructose. This catalytic reaction was found to take place with very different velocities when different acids were used, and Löwenthal and Lenssen,[1] as early as 1862, used this reaction to measure the relative activities of acids. They determined the velocities with which a number of acids invert sugar, and also the effect of the presence of a number of substances on the velocity of inversion. Their work was, however, shown to be open to certain objections, and Ostwald[2] carried out an extensive investigation on the velocity with which cane sugar is inverted by different acids, using the polarimeter to measure the amount of inversion.

He calculated the inversion coefficients by the method with which we are now familiar, —

$$CB = \frac{1}{t} \ln \frac{A}{A-x},$$

and showed that they are identical with the activity coefficients of the acids used. That such is the case will be seen after we study methods for measuring the activity coefficients directly. A few of the results obtained for the inversion coefficients of some of the more common acids are given below, hydrochloric acid being taken as unity: —

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[1] *Journ. prakt. Chem.* **85**, 321, 401 (1862).

[2] *Ibid.* [2], **29**, 385 (1884).

	INVERSION COEFFICIENTS
Hydrochloric acid	1.000
Nitric acid	1.000
Ethylsulphuric acid	1.000
Hydrobromic acid	1.114
Chloric acid	1.035
Benzenesulphonic acid	1.044
Sulphuric acid	0.536
Formic acid	0.0153
Acetic acid	0.0040
Monochloracetic acid	0.0484
Dichloracetic acid	0.271
Trichloracetic acid	0.754
Oxalic acid	0.1857
Succinic acid	0.00545
Citric acid	0.0172
Phosphoric acid	0.0621
Arsenic acid	0.0481

(*B*) **Saponification of Methylacetate.**— Methylacetate and similar esters in the presence of water at ordinary temperatures, undergo a slow decomposition into the acid and alcohol. If a strong acid is present, the decomposition takes place much more rapidly; indeed, its velocity may be increased a hundred times, or even more than this.

The acid which is added to the ester does not undergo any change. It acts catalytically. The active mass of the ester is the only substance which changes as the reaction proceeds, and, therefore, the reaction is of the first order. The constant is —

$$CB = \frac{1}{t} \ln \frac{A}{A - x}.$$

This equation was tested experimentally by Ostwald,[1] who used this reaction to measure the relative activities of acids, and BC was found to be a constant for this reaction through a long interval of time.

Ostwald worked out the velocity coefficients of a large number of acids by means of the above reaction. A few of his results are given below: —

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[1] *Journ. prakt. Chem.* [2], **28**, 449 (1883).

	VELOCITY COEFFICIENTS
Hydrochloric acid	1.000
Nitric acid	0.915
Ethylsulphuric acid	0.987
Hydrobromic acid	0.983
Chloric acid	0.944
Benzenesulphonic acid	0.991
Sulphuric acid	0.541
Formic acid	0.0131
Acetic acid	0.00345
Monochloracetic acid	0.0430
Dichloracetic acid	0.2304
Trichloracetic acid	0.6820
Oxalic acid	0.1746
Succinic acid	0.00496
Citric acid	0.01635

A comparison of the velocity coefficients obtained by the methyl-acetate method, with the inversion coefficients obtained by the method involving the inversion of cane sugar, shows a general agreement between the two sets of values. Both of these methods can be used to measure the relative activities of substances.

(*C*) **The Decomposition of Amides.** — Another dynamic method has been used to measure the relative activities of acids. This involves the action of acids on amides. Water alone decomposes an amide like acetamide, in the sense of the following equation: —

$$CH_3CONH_2 + H_2O = CH_3COONH_4.$$

This reaction, however, takes place very slowly.

If an acid is added the velocity of the reaction is increased, and very greatly increased if the acid is strong. In the presence of an acid the reaction takes place as follows: —

$$CH_3CONH_2 + H_2O + HCl = CH_3COOH + NH_4Cl,$$

both the acid and amide being used up.

Since the active masses of two substances undergo change, we have a reaction of the second order; and we have seen that in a reaction of the second order the activity coefficients are related as the square roots of the velocity coefficients.

Since equivalent quantities of acid and amide are used up in the reaction, the constant is —

$$CB = \frac{1}{t}\,\frac{x}{A-x}.$$

Although side reactions come into play somewhat as the above reaction proceeds, their influence at the outset is small, and very nearly the true velocity coefficients for the different acids can be obtained by studying the decomposition of amides at the very outset of the reaction.

The following are the velocity coefficients for a number of acids, obtained by means of the method involving the decomposition of acetamide:—

	VELOCITY COEFFICIENTS
Hydrochloric acid	1.000
Nitric acid	0.955
Hydrobromic acid	0.972
Sulphuric acid	0.547
Formic acid	0.00532
Acetic acid	0.000747
Monochloracetic acid	0.0295
Dichloracetic acid	0.245
Trichloracetic acid	0.670
Oxalic acid	0.169
Tartaric acid	0.0121
Succinic acid	0.00195
Citric acid	0.00797
Phosphoric acid	0.0449

If we compare the results obtained by the amide method with those obtained by saponifying an ester, we see that the two sets of values agree for the strong acids, although quite different temperatures were used in the two sets of experiments. For the weak acids the results obtained by the amide method are the smaller, and this is just what we would expect, since the presence of the neutral salt formed in the reaction diminishes the velocity with which the amide is decomposed.

The three dynamic methods give, then, essentially the same results for the activity coefficients of acids; we shall now study the application of one dynamic method to the relative activities of bases.

(*D*) **Saponification of Esters by Bases.**—An ester like ethylacetate is saponified by a base in terms of the following equation:—

$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH.$$

The reaction was first used by Warder[1] to measure the relative activities of bases, and afterward more extensively applied by Reicher.[2]

A few of the velocity coefficients of the more common bases are given below:—

[1] *Amer. Chem. Journ.* **3**, 340 (1882).

[2] *Lieb. Ann.* **228**, 257 (1885).

	VELOCITY COEFFICIENTS
Potassium hydroxide	2.298
Sodium hydroxide	2.307
Ammonium hydroxide	0.011
Barium hydroxide	2.144
Strontium hydroxide	2.204

The most striking feature in the above results is that ammonia is such a weak base in comparison with potassium or sodium hydroxide. We shall see that this result is confirmed by other methods.

We shall now leave the dynamic methods of measuring relative activities, and pass to the static or equilibrium methods.

The Equilibrium Methods of measuring Relative Activities. (1) Thermochemical Method. — These methods, as already stated, allow the substances whose relative activities are to be measured to come to equilibrium, and then determine the conditions of the equilibrium. If the reaction is heterogeneous, a solid entering into the reaction or being formed as the result of the reaction, it is a simple matter to determine the conditions which exist when equilibrium is established. It is only necessary to determine the amount of the solid present, or to separate the heterogeneous constituents, and determine their amounts by any of the ordinary chemical methods. If, on the other hand, the reaction is homogeneous, the problem of determining the amounts of the constituents when equilibrium is established is far more difficult. It frequently happens that the constituents cannot be readily separated by chemical means, and resort must be had to some indirect method of determining the quantities present. The change in some physical property which can be readily measured has been frequently utilized to determine the conditions of equilibrium in a homogeneous reaction.

Julius Thomsen used the thermal change, or heat tone of a reaction, to measure the relative activities of the substances which take part in the reaction. If the heat of neutralization of a base, say sodium hydroxide, by an acid, say hydrochloric acid, is different from the heat of neutralization of the same amount of the same base under the same conditions, by a different acid, say sulphuric acid, it is quite simple to determine the division of the base between the two acids by means of the heats of neutralization. We must know the heat of neutralization of the first acid by the base, also the heat of neutralization of the second acid by the base, and in addition the heat set free when both acids are brought simultaneously into contact with the base. Let us call these quantities, respectively, N_1, N_2, and N_3. If all of the base went to the first acid, N_3 would be equal to N_1. If all of the base went to the second acid, N_3 would be equal to N_1. But if part of the base goes to one acid and part to the other, as is always the case, N_3 will lie somewhere between N_1 and N_2. By simple proportion we can tell at once how much of the base has gone to each acid, and thus we have the relative activities of the two acids. In practice one acid is allowed to act on the salt of the other acid, but the principle is as indicated above.

We can, of course, reverse the above procedure, and neutralize one acid by two bases separately, and then by both bases simultaneously, and from the data thus obtained calculate the relative strengths of the bases. In this way tables of the relative strengths or activities of acids and bases can be worked out by thermochemical measurements. In such investigations, however, side reactions may come into play, and such must of course be taken into account wherever they appear.

It should be mentioned again in connection with this method, that thermochemical measurements are difficult to make with even a fair degree of accuracy, and this method is never used to-day, since, as we shall see, far simpler and more accurate methods are now available for measuring chemical activity.

(2) Volume-chemical Method. — Just as chemical reactions are accompanied by thermal change, so, also, are they accompanied by change in volume. When a solution of an acid is brought in contact with a solution of a base, the resulting volume is different from the sum of the volumes of the two solutions. There is usually a contraction in volume under such conditions.

Ostwald[1] has utilized the change in volume produced in chemical reactions to determine the relative activities of acids and bases, in a manner strictly analogous to that of Thomsen just described. When a given base is neutralized by different acids, different changes in volume result. Ostwald has utilized these differences to determine just how much of a base goes to each acid, or of an acid to each base; and thus the relative activities of acids and bases. It is only necessary to know the change in volume when the base is neutralized by one acid, the change in volume when the base is neutralized by the second acid, and the change in volume when the base is neutralized by both acids simultaneously.

In practice we do not proceed as described above, but allow one acid to act on the salt of the other acid. The above procedure was described because it is exactly the same in principle as that which was actually employed in the experiment, and is far simpler to comprehend.

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[1] *Journ. prakt. Chem.* [2], **18**, 328 (1878).

The volume-chemical method is greatly to be preferred to the thermochemical, because of the ease with which it can be carried out. It is not necessary to measure the change in volume; it is sufficient to measure the change in density or specific gravity, and this can be done very readily by any of the ordinary specific gravity methods. The method employed by Ostwald consists in weighing the solution in a modification of the Sprengel pycnometer devised by himself. The method when carried out in this manner becomes one of the simplest laboratory methods of which we can conceive.

It has been stated that in both of the above methods one acid is allowed to act on the salt of another acid, and from the division of the base between the two acids the relative strengths of the acids determined. At first thought this statement is liable to lead to confusion. It will be recalled at once that when sulphuric acid acts on a dry chloride, like sodium chloride, practically all of the hydrochloric acid is displaced by the sulphuric acid; and when sulphuric acid acts on dry nitrates, practically all of the nitric acid is driven out. This might be thought to indicate that sulphuric acid is infinitely strong with respect to hydrochloric or nitric acid.

Again, when hydrogen sulphide is allowed to act on a soluble chloride or nitrate of a heavy metal, the insoluble sulphide is precipitated, and in many cases quantitatively. From this it might be concluded that hydrogen sulphide is a much stronger acid than hydrochloric or nitric.

A moment's thought will show that these conclusions are necessarily erroneous. The error lies in not taking into account the fact that, under these conditions, a volatile compound is formed in the first case and escapes from the field of action, its active mass being, therefore, reduced to zero; while in the second case an insoluble compound is formed and separates from the solution.

In order to test the relative activities of two acids or bases, by allowing one to act on the salt of the other, the two acids or bases in question must be under comparable conditions, *i.e.* the active masses of both must be equal. This can be secured by working with solutions where everything is in solution before the reaction takes place, and remains in solution after the reaction is over and equilibrium is established. If we work with equivalent quantities of substances, under these conditions their active masses are equal, and the division of the base between two acids, or of the acid between two bases, gives at once the relative activities of the acids or bases in question.

(3) **Other Equilibrium Methods of measuring Relative Activities.** — The two methods discussed above utilize, respectively, the thermal change and the volume change produced in chemical reactions. In a similar manner, the change in any other physical property produced by chemical action may be used to determine the conditions which exist when equilibrium has been established. A number of other properties have been utilized for this purpose, such as the change in the refractive power of the solution, in its color, in its power to rotate the plane of polarized light, etc.; but no new principle is involved in these methods, and many of them are of limited applicability. These will not be discussed in detail, since the equilibrium methods, as well as the dynamic methods of measuring relative chemical activities, have, in general, given place in the last few years to a method which is more accurate and far easier to carry out in practice than any method thus far considered. This is the method with which we are already familiar, based upon the electrical conductivity of substances.

The Conductivity Method of measuring Chemical Activity. — Since it has been shown that chemical activity is due only to ions, it is but necessary to determine the relative number of ions present in order to determine chemical activity. The problem of measuring chemical activity reduces itself, then, to the measurement of electrolytic dissociation.

The conductivity method of Kohlrausch and its application to the measurement of electrolytic dissociation have been considered at sufficient length; it only remains to discuss some of the results which have been obtained.

The strong mineral acids are dissociated to just about the same extent. These include hydrochloric, nitric, hydrobromic, chloric, and a few others. The strong bases, such as sodium, potassium, calcium, lithium, and rubidium hydroxides, are dissociated to just about the same extent, and to about the same extent as the strong acids under the same conditions. The salts are, in general, strongly dissociated compounds. They are dissociated to very nearly the same extent as the strong acids and bases. There are, however, some exceptions among the salts; those of cadmium and mercury, and zinc to a less degree, are dissociated much less than the other salts. Indeed, some of the salts of mercury, such as the chloride and cyanide, are scarcely dissociated at all. The above statement, nevertheless, applies to most of the salts, including those of very weak acids, such as carbonic and hydrocyanic, potassium carbonate and cyanide being quite strongly dissociated compounds.

Since dissociation and chemical activity are proportional, when we speak of a compound as being strongly dissociated we mean one whose chemical activity is great. Since conductivity has been used to measure chemical activity, we use the terms "dissociation" and "chemical activity" as synonymous.

When we turn to the organic acids and bases, we find nearly all degrees of activity represented. Some of the organic acids as formic, oxalic, trichloracetic, and the like are quite strong; while acids like acetic, succinic, citric, hydrocyanic, are very weakly dissociated compounds.[1]

Similarly, when we deal with the organic bases, we find that many of the substituted ammonias are strongly dissociated substances, while ammonia itself is a very weak base.

When we were studying the conductivity method itself, and its application to electrolytes, we saw that the molecular conductivity and, consequently, the dissociation increased with the dilution of the solution. In order that the results obtained by this method for different substances should be comparable, we must, therefore, work at the same dilutions, and this is always taken into account in applying the conductivity method to the measurement of chemical activity. The magnitude of the influence of dilution will be seen when we recall that a normal solution of a strong acid, base, or salt is about eighty per cent dissociated; while a thousandth's normal is completely dissociated.

The importance of the dilution laws is especially great, in connection with the application of the conductivity method to the measurement of chemical activity. Take the law of Rudolphi, $\frac{\alpha^2}{(1-\alpha)\sqrt{v}} =$ constant, which applies to strongly dissociated electrolytes. The value of the constant is a measure of the chemical activity of the substance.

Take the weakly dissociated compounds — the organic acids and bases — to which the dilution law of Ostwald applies. The value of the constant in the equation, $\frac{\alpha^2}{(1-\alpha)v} =$ constant, has been used as a direct measure of the strength of the acid and base, as we have seen.

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[1] For details in connection with the strengths of organic acids and bases see Ostwald: *Ztschr. phys. Chem.* **3**, 170, 241, 369 (1889); and Bredig: *Ibid.* **13**, 289 (1894).

In comparing the strengths of organic acids and bases by means of the conductivity method, we can measure the dissociations at the same dilutions and compare the results, or we can measure the dissociations at any dilutions, substitute the values in the Ostwald dilution law, and compare the values of the constants obtained. The latter mode of procedure is usually adopted because it is simpler and more convenient.

The same remarks apply to the strongly dissociated compounds.

We thus see how the conductivity method can be used to measure chemical activity; we shall now learn what influence composition and constitution exert on the chemical activities of substances.

EFFECT OF COMPOSITION AND CONSTITUTION ON CHEMICAL ACTIVITY

Composition as conditioning Acidity. — We have already seen from the periodic system what elements are in general acid-forming, and what are base-forming. In this connection we should look a little more closely into this question, and inquire not only into the qualitative influence of the different elements, but the magnitude of the influence which they exert. This is now quite a simple matter, since we have such convenient methods for measuring chemical activity.

If we look at the history of acids, we shall find that for a long time it was thought that acid properties are due entirely to the presence of oxygen. Indeed, the name of this element means acid-former. According to the earlier views it was impossible to have an acid without the presence of oxygen. So firmly rooted did this idea become, that when hydrochloric acid was discovered it was thought that it must contain oxygen, notwithstanding the fact that no oxygen could be detected in its molecule. The only possibility of the presence of oxygen was that it was combined with the chlorine, so it was said that chlorine must contain oxygen and be an oxide, and not an element. It was regarded as the oxide of an unknown element "murium," whence the name muriatic acid.

We know to-day that oxygen as such has nothing to do directly with acidity. The cause of acid properties is the hydrogen ion. Wherever we have hydrogen ions we have acid properties, and wherever we have acid properties we have hydrogen ions. The strength or activity of acids depends entirely upon the number of hydrogen ions present in their solutions — upon the dissociation.

If acid properties depend entirely upon the hydrogen ions, how do other elements affect acidity at all? W acid-forming element?

Elements other than hydrogen do not af they may affect it very greatly indirectly, in or retard the dissociation which yields the we say that an element is acid-forming, w facilitates the dissociation of hydrogen from it is present.

If we examine the strength of acids in t conceptions, we shall find some surprising well-known compounds. Take first the *fou* been accustomed to regard them all as very the exception of hydriodic acid, which is son regarded them as about of equal strength. conductivities at the same dilutions, we find

VOLUMES	HCl	HBr
	μ_v	μ_v
4	343	354
16	362	367
256	378	380
1024	380	380
4096	376	372

We see that hydrochloric, hydrobromic, of about the same strengths for all dilutions thousand; but hydrofluoric acid is very mu the more concentrated solutions. As the d the hydrofluoric acid continues to dissociat nearly to the values of the other acids.

Effect of Oxygen and Sulphur on Acidity. very weak acids,—hydrogen sulphide and h see how the introduction of oxygen into the the other affect the acidity.

Hydrogen sulphide is a very weak acid in by the few conductivity measurements whic Ostwald.[1] When oxygen is introduced into have first sulphurous acid and then sulphu the influence of oxygen in the molecule may ties of hydrogen sulphide, sulphurous acid, and sulphuric acid, as far as they have been determined at comparable dilutions, are given below: —

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[1] *Journ. prakt. Chem.* 32, 300 (1885);

VOLUMES	H_2S	H_2SO_3	H_2SO_4
	μ_v	μ_v	μ_v
16	0.70	—	407.0
32	0.91	177.5	448.0
256	—	279.0	582.0
1024	—	324.7	649.0

Sulphurous acid is obviously much stronger than hydrogen sulphide, and sulphuric acid[1] much stronger than sulphurous. The introduction of oxygen into the molecule of hydrogen sulphide has thus very greatly increased the acidity, which is the same as to say has greatly facilitated the dissociation of hydrogen from the molecule.

Let us see what influence the introduction of sulphur into the molecule of hydrocyanic acid has on its acidity. Comparing the conductivities of hydrocyanic acid and sulphocyanic acid, as determined by Ostwald,[2] we have: —

VOLUMES	HCN	HSCN
	μ_v	μ_v
4	0.33	337
8	0.38	345
16	0.43	352
32	0.46	358

The introduction of sulphur into the molecule of hydrocyanic acid has increased its acidity several hundred times. Indeed, hydrocyanic acid is scarcely an acid at all, while sulphocyanic acid is to be ranked among the very strong acids, as will be seen from the results of the conductivity measurements.

It might be concluded from the above results that the introduction of oxygen or sulphur into a molecule always increased the acidity. Such might be the case, but the data thus far examined are too few to justify any such conclusion. Let us examine a number of other cases. Take the acids of phosphorus, where we have a number of members differing by an oxygen atom.

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[1] If the molecular conductivities of sulphuric acid are compared with those of hydrochloric acid at the same dilutions, it will be seen that the former are much the greater. This is because sulphuric acid splits off two hydrogen ions, both of which take part in the conductivity. It is only a little more than half as strong as hydrochloric acid.

[2] *Loc. cit.*

VOLUMES	H_3PO_2	H_3PO_3	H_3PO_4
	μ_v	μ_v	μ_v
2	131	121	60
8	194	175	90
32	264	241	146
128	314	298	225
512	339	329	297
2048	346	339	335

Here the acidity continually decreases as the amount of oxygen increases, which is exactly the opposite of what we found with the acids derived from hydrogen sulphide by the introduction of oxygen. The evidence bearing upon the effect of oxygen on acidity seems conflicting. What conclusion are we to draw?

If we examine a great number of cases, we find that the introduction of oxygen usually increases the acidity; sometimes it has little or no influence on the acidity of the compound, and in a few cases like the above it actually diminishes the acidity of the compound into which it enters.

An examination of the acids into which sulphur enters shows that the effect of the presence of sulphur is to increase acidity. Some other influence, as change in the constitution of the compound produced by the introduction of sulphur, may offset the influence of the sulphur atom; but this is of course a different matter, and does not detract from the truth of the above statement.

Organic Acids and their Substitution Products. — Thus far we have considered mainly inorganic acids. The effect of composition on the strength of organic acids can be seen best by studying homologous series of the fatty acids, and then some of the substitution products of these acids. Take first the formic acid series, and compare the molecular conductivities of the first five members at the same dilutions: —

VOLUMES	FORMIC ACID	ACETIC ACID	PROPIONIC ACID	BUTYRIC ACID	VALERIC ACID
	μ_v	μ_v	μ_v	μ_v	μ_v
8	15.22	4.34	3.65	3.80	—
32	29.31	8.65	7.36	7.70	7.94
128	55.54	16.99	14.50	15.27	15.70
1024	134.70	46.00	38.73	40.62	41.90

These results show that formic acid is much stronger than any succeeding member of the series. The acidity of the following members does not change very appreciably with increase in the complexity of the molecule; there is, perhaps, a slight decrease in the acidity as the molecule becomes more complex.

Take the first three members of the oxalic acid series, — oxalic, malonic, and succinic acids, — and compare their conductivities in a similar manner: —

VOLUMES	OXALIC ACID	MALONIC ACID	SUCCINIC ACID
	μ_v	μ_v	μ_v
16	—	53.07	11.40
128	324	128.5	31.28
512	364	208.8	59.51
2048	409	294.5	109.5

In this series the decrease in acidity with increase in complexity is very marked indeed. Oxalic acid is much stronger than malonic, and malonic is a much stronger acid than succinic.

Turning to the substituted acids of the formic acid series Ostwald[1] has measured the conductivities of the *chloracetic acids* and of *monobromacetic acid*. His results are given in the following table, together with those of acetic acid itself for the sake of comparison: —

VOLUMES	ACETIC ACID	MONOCHLORACETIC ACID	DICHLORACETIC ACID	TRICHLORACETIC ACID	MONOBROMACETIC ACID
	μ_v	μ_v	μ_v	μ_v	μ_v
32	8.65	72.4	253.1	323.0	68.7
128	16.99	127.7	317.5	341.0	122.3
512	32.2	205.8	352.2	353.7	199.2
1024	46.0	249.2	360.1	356.0	241.2

From acetic acid and its chlorsubstitution products we see the effect of substituting hydrogen in the methyl group by chlorine. The acidity is greatly increased by the presence of the first chlorine atom; it is still further increased by the presence of the second chlorine atom, and trichloracetic acid is a very strong acid indeed. Bromine, like chlorine, also greatly increases the acidity of acetic acid, and to nearly the same extent.

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[1] *Ztschr. phys. Chem.* **3**, 176–178 (1889).

Ostwald[1] next studied *the effect of introducing an oxygen* *the radical* on the acidity of the compound. Take acetic its monoxygen derivative, glycolic acid:—

Volumes	Acetic Acid	Glycolic A
	μ_v	μ_v
32	8.65	24.79
128	16.99	47.50
1024	46.0	116.70

The introduction of an oxygen atom into acetic acid incre acidity many times.

Take propionic acid and compare its acidity with its derivatives:—

Volumes	Propionic Acid	Lactic Acid	β-Oxyprop
	μ_v	μ_v	μ
16	5.21	16.46	7.
128	14.50	44.47	21.
1024	38.73	109.70	57.

Here we have two monoxy-derivatives to deal with, de upon which group (CH_3 or CH_2) the oxygen enters. If it en CH_2 group, the acidity is greatly increased; if the CH_3 gr acidity is increased, but not to the same extent. Here we en the effect of constitution on acidity; but more of this later.

Turning next to the oxysuccinic acids, we have the mo derivative or the malic acids, and the dioxy-derivative or acids. Ostwald[2] has also measured the conductivities of th stances, and the following data are taken from his results:—

Volumes	Succinic Acid	Malic Acid	*d*-Tartar
	μ_v	μ_v	μ
32	16.03	37.90	57.
128	31.28	71.52	106.
512	59.51	128.10	184.
2048	109.50	313.0	291.1

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[1] *Ztschr. phys. Chem.* **3**, 183 (1889).

[2] *Ibid.* **3**, 370–372 (1889).

The introduction of oxygen into succinic acid also increases the acidity to a marked extent. The introduction of one oxygen atom more than doubles the acidity, while the introduction of a second oxygen atom still further increases the acidity, especially in the more concentrated solutions.

The influence of the *presence of the nitro group* is seen by comparing the conductivity of an acid like benzoic acid with the conductivity of mononitro benzoic acid:—

Volumes	Benzoic Acid	o-Nitrobenzoic Acid
	μ_v	μ_v
128	29.70	205.3
256	42.20	246.1
512	57.61	283.3
1024	78.94	312.3

The presence of the nitro group greatly increases the acidity of the compound into which it enters.

The presence of the amido group has the opposite effect, as we would expect. Comparing the conductivities of benzoic acid and *p*-amidobenzoic acid, we see that this conclusion is justified by the facts:—

Volumes	Benzoic Acid	p-Amidobenzoic Acid
	μ_v	μ_v
64	21.39	7.53
256	42.20	16.34
1024	78.94	35.01

Constitution as conditioning Acidity.—We have seen one example of the effect of constitution on acid properties. Lactic acid and *b*-oxypropionic acid are isomeric, having the same composition; but the acidity of the former is more than double that of the latter. We shall now study other isomeric substances to see whether the influence of constitution on acidity is general.

Take the two acids having the composition C_3H_7COOH,—butyric and isobutyric acids,—and comparing their conductivities at the same dilutions, we have:—

VOLUMES	BUTYRIC ACID	ISOBUTYRIC ACID
	μ_v	μ_v
16	5.46	5.31
64	10.86	10.68
256	21.33	20.85
1024	40.62	39.97

The acidity of these two isomeres is very nearly the same, constitution having but little influence in these cases.

Take next the two isomeric monoxy-derivatives of succinic acid,— malic and inactive malic acids: —

VOLUMES	MALIC ACID	INACTIVE MALIC ACID
	μ_v	μ_v
64	53.08	53.5
512	128.1	128.6
2048	213.0	212.2

Constitution seems to have little or no influence in the above cases.

Comparing the acidities of the dihydroxysuccinic acids, Ostwald[1] has determined the conductivities of the three isomeric substances, — dextrotartaric acid, lævotartaric acid, and racemic acid: —

VOLUMES	*d*-TARTARIC ACID	*l*-TARTARIC ACID	RACEMIC ACID
	μ_v	μ_v	μ_v
32	57.6	57.6	57.6
128	106.2	105.6	106.0
512	184.5	183.2	182.5
2048	291.1	289.5	288.0

Here, again, constitution has little or no influence on the acidity of the isomeric substances.

We shall take up next an *entirely different kind of isomerism*, dependent upon the arrangement of the atoms in space (*stereoisomerism*), and see what influence the different spatial configurations have on the strength of the acid.

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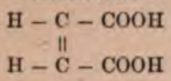
[1] *Ztschr. phys. Chem.* **3**, 371–372 (1889).

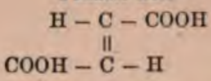
Take the two acids having the composition $C_2H_2(COOH)_2$, — maleïc and fumaric acids. In terms of stereochemistry and the conception of the tetrahedral carbon atom, these acids are to be represented by the following formulas: —

Maleïc Acid



$$\begin{array}{l} H - C - COOH \\ \quad\;\; \| \\ H - C - COOH \end{array}$$

Fumaric Acid



$$\begin{array}{r} H - C - COOH \\ \| \quad\quad\quad\;\; \\ COOH - C - H \end{array}$$

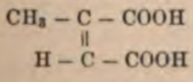
In maleïc acid the two hydrogen atoms and, similarly, the two carboxyl groups are on the same side of the molecule. In fumaric acid, hydrogen is opposite carboxyl. It is very interesting to see what influence this difference in configuration would have on the acidity of the compounds. Ostwald[1] has measured the conductivity of these acids: —

Volumes	Maleïc Acid	Fumaric Acid
	μ_v	μ_v
32	168.0	56.4
128	245.0	104.5
512	312.0	179.5
2048	350.0	280.2

The acidity of the maleïc acid is obviously very much the greater. This is probably connected in some way with the proximity of the hydrogen atoms, which form ions and give the acid properties to the compounds.

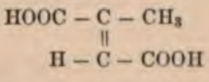
Let us take another example of stereoisomeric substances, and see what influence configuration or spatial relation has on their acidity. According to Wislicenus,[2] citraconic and mesaconic acids are isomeric in the same sense as maleïc and fumaric acids: —

Citraconic Acid



$$\begin{array}{r} CH_3 - C - COOH \\ \| \quad\quad\quad\;\; \\ H - C - COOH \end{array}$$

Mesaconic Acid



$$\begin{array}{r} HOOC - C - CH_3 \\ \| \quad\quad\;\; \\ H - C - COOH \end{array}$$

In citraconic acid the two carboxyl groups are on the same side of the molecule, while in mesaconic acid they are on different sides.

The following comparison of the conductivities of the two acids shows that they have very different strengths: —

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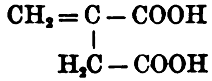
[1] *Ztschr. phys. Chem.* **3**, 380 (1889).

[2] *Abh. d. Kgl. Sächs. Ges. d. Wis.* **24**, 37 (1887).

Citraconic Acid		
Volumes	μ_v	Volumes
68.3	135.0	47.95
136.5	172.2	191.8
546.0	253.2	767.2
2184.0	315.3	3068.4

Citraconic acid is, obviously, much the stro

There is a third substance having the sa above, known as itaconic acid. It has, howev methylenesuccinic acid, having the constituti formula —



$$\begin{array}{l} CH_2 = C - COOH \\ \qquad\quad | \\ \qquad H_2C - COOH \end{array}$$

Its acidity is less than even that of mes seen by the following conductivity results: —

Volumes

11.11 . . . .

44.44 . . . .

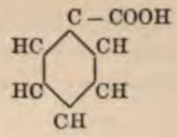
177.8 . . . .

711.1 . . . .

1422.0 . . . .

We shall now turn to another kind of ison the aromatic compounds, and see what effect t in constitution has on the properties of the su

The most probable formula for the *constit sents its molecule as a hexagon,* with the si corners of the hexagon. In terms of this have three kinds of disubstitution products, three are known: ortho, where the two su joining corners of the hexagon; para, where corners; and meta, where there is one corner question which arises in this connection is the position occupied by an atom or group h the compound? Take as an example benz structure represented thus: —



If we replace one of the five hydrogen atoms by a hydroxyl group, or what is the same thing introduce an oxygen atom into the molecule, what influence on the acidity would the position of the oxygen atom have? This is answered by comparing the acidity of benzoic acid with that of ortho, meta, and para oxybenzoic acids, respectively. The following data are taken from the work of Ostwald:[1] —

VOLUMES	BENZOIC ACID	*o*-OXYBENZOIC ACID SALICYLIC ACID	*m*-OXYBENZOIC ACID	*p*-OXYBENZOIC ACID
	μ_v	μ_v	μ_v	μ_v
64	21.39	80.1	25.67	14.83
256	42.20	141.9	49.36	29.35
1024	78.94	224.1	91.63	56.25

The position of the oxygen atom has thus a very marked influence on its effect on the acidity of benzoic acid. In the ortho position it increases the acidity more than three times; in the meta position the acidity is increased but only slightly, while the presence of the oxygen in the para position actually decreases the acidity of benzoic acid.

Let us examine next the effect of chlorine in the three positions: —

VOLUMES	BENZOIC ACID	*o*-CHLORBENZOIC ACID	*m*-CHLORBENZOIC ACID	*p*-CHLORBENZOIC ACID
	μ_v	μ_v	μ_v	μ_v
64	21.39	89.2	—	—
256	42.20	156.1	64.3	—
1024	78.94	238.7	116.2	125

Chlorine in the ortho position has the greatest influence, in the para position an intermediate influence, while in the meta position it has the least influence. This is not the order with respect to the influence exerted, which was observed with oxygen.

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[1] *Ztschr. phys. Chem.* 3, 241 (1889).

Take the nitrobenzoic acids:—

VOLUMES	BENZOIC ACID	*o* NITROBENZOIC ACID	*m*-NITROBENZOIC ACID	*p*-NITROBENZOIC ACID
	μ_v	μ_v	μ_v	μ_v
128	29.70	205.3	67.5	—
256	42.20	246.1	90.9	97.0
1024	78.94	312.3	157.6	164.7

The nitro group increases the acidity of benzoic acid when in any of the three positions. It has the greatest influence in the ortho position, less in the para, and the least influence in the meta position. Take, finally, the effect of position on the influence of the amido group:—

VOLUMES	BENZOIC ACID	*o*-AMIDOBENZOIC ACID	*m*-AMIDOBENZOIC ACID	*p*-AMIDOBENZOIC ACID
	μ_v	μ_v	μ_v	μ_v
64	21.39	7.21	22.16	7.53
256	42.20	16.11	44.39	16.34
1024	78.94	33.51	88.30	35.01

The amido group in the ortho position and in the para position greatly diminishes the acidity of benzoic acid, while the amido group in the meta position has little or no influence on the acidity of benzoic acid.

It is obvious from the above results that position has a marked effect on the influence of atoms and groups on the acidity of compounds. No wide-reaching generalization, which is free from exceptions, has been arrived at, connecting these phenomena. It may be said in general that the greatest influence is exerted in the ortho position, while the smallest influence is shown by the substituent in the meta or para position.

We have studied in this chapter the influence of composition on acidity, and also the influence of constitution on acidity. Let us now see what influence composition and constitution have on the strength of bases.

Composition as conditioning Basicity. — We have seen that the cause of acidity is the presence of hydrogen ions, and an acid is strong or weak in proportion to the number of hydrogen ions present — in proportion to its dissociation.

In an analogous manner, the cause of basicity is the presence of hydroxyl ions. Wherever we have hydroxyl ions we have basic property, and wherever we have basic property we have hydroxyl ions. A base is strong or weak just in proportion to the number of hydroxyl ions present, *i.e.* in proportion to its dissociation.

The strongest of all bases, as we have learned, are the hydroxides of the alkali metals, — potassium, sodium, calcium, lithium, and rubidium hydroxides. These are dissociated to just about the same extent as the strongest mineral acids, under the same condition of concentration.

When we come to ammonium hydroxide, we find a base which is incomparably weaker than those to which we have just referred. That this may be fully appreciated, the molecular conductivities of a few solutions of ammonium hydroxide are compared with the molecular conductivities of the corresponding solutions of potassium hydroxide, the measurements being made at the same temperatures: —

VOLUMES	POTASSIUM HYDROXIDE	AMMONIUM HYDROXIDE
	μ_v	μ_v
1	171.8	0.84
10	198.6	3.1
100	212.4	9.2
1000	211.0	26.0

In normal solution, potassium hydroxide is nearly two hundred times as strong as ammonium hydroxide; as the dilution increases, the strength of ammonium hydroxide, relative to potassium hydroxide, increases, until at a dilution of 1000 litres, where potassium hydroxide is completely dissociated, ammonium hydroxide is about one-eighth as strong as potassium hydroxide.

Ammonium hydroxide is an example of the way in which physical chemistry has corrected errors in chemistry, which have persisted for a long time. Ammonium hydroxide was regarded as a very strong base, and there was no purely chemical means of correcting the error. It precipitated most of the substances with which potassium hydroxide formed a precipitate; it acted vigorously upon the mucous membrane of the throat and nose, and altogether behaved like a very strong base. It remained for a physical chemical method — the conductivity method — to show that it is relatively a weak base, by measuring the relative number of hydroxyl ions present.

The hydroxides of the alkaline earths, — calcium, strontium, and barium, are very strong bases, but not as strong as the hydroxides of the alkalies. Halving the molecular conductivities of the former, and comparing these values with the molecular conductivities of potassium hydroxide under the same conditions, we have: —

VOLUMES	KOH	$\frac{1}{2}$ $Ca(OH)_2$	$\frac{1}{2}$ $Sr(OH)_2$	$\frac{1}{2}$ $Ba(OH)_2$
	μ_v	μ_v	μ_v	μ_v
32	207	—	190	193
64	210	190	197	201
256	214	220	209	216
1024	212	—	212	220

The relative strengths of the two sets of hydroxides are obvious from the above values.

If we go farther and examine the hydroxides of the heavy metals, we would find that most of them are so slightly soluble that their conductivities cannot be measured satisfactorily. We would also find that some hydroxides, like aluminium and zinc, are acid under one set of conditions and basic under other conditions. In the presence of a strong acid they are basic, and in the presence of a strong base they are acidic.

It may seem difficult at first to account for these facts in the light of the present simple conceptions of acid and base; but they really present no difficulty. A substance like aluminium hydroxide in the presence of a strong acid dissociates like the alkaline hydroxides, yielding hydroxyl ions which give it its basic properties. In the presence of a strong base it dissociates yielding hydrogen ions, and a complex anion containing aluminium, oxygen, and probably some hydrogen. The way in which the molecule breaks down into ions may be conditioned by the nature of the substance with which it is in contact.

Organic Bases. — The most accurate work on the conductivity of the organic bases we owe to Bredig,[1] who carried out this elaborate series of measurements in connection with his dissertation in Ostwald's laboratory and under his guidance. Let us examine first the effect of composition on basicity among the primary amines, by comparing some of the members of the homologous series, — methylamine, ethylamine, etc.: —

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[1] *Ztschr. phys. Chem.* **13**, 289 (1894).

VOLUMES	AMMONIA	METHYLAMINE	ETHYLAMINE	PROPYLAMINE
	μ_v	μ_v	μ_v	μ_v
8	3.20	14.1	13.8	12.3
32	6.28	27.0	27.0	23.9
128	12.63	49.5	49.4	44.7
256	17.88	65.4	65.6	59.6

Methylamine is a much stronger base than ammonia itself, showing that the replacement of one hydrogen atom by a methyl group has greatly increased the basicity. Ethyl has just about the same influence as methyl, while propyl has a slightly smaller influence.

The question which would next arise is what influence would the replacement of a second hydrogen atom by a radical have on the basicity? This can be answered by studying the series of secondary amines: —

VOLUMES	DIMETHYLAMINE	DIETHYLAMINE	DIPROPYLAMINE
	μ_v	μ_v	μ_v
8	16.1	19.1	16.6
32	31.0	37.1	33.1
128	57.2	67.1	60.0
256	75.4	86.6	77.6

Dimethylamine is slightly stronger than monomethylamine, and, similarly, for diethyl- and dipropyl-amines.

We can go farther and introduce a third group into ammonia, giving the tertiary ammonium bases. It is of interest to see what influence the third group has on the basicity: —

VOLUMES	TRIMETHYLAMINE	TRIETHYLAMINE	TRIPROPYLAMINE
	μ_v	μ_v	μ_v
8	4.95	13.3	—
32	10.2	27.1	—
128	20.0	50.0	—
258	27.5	66.4	60

The introduction of the third radical diminishes the basicity very considerably.

We can, however, go one step farther and introduce a fourth radical into ammonia, giving the quaternary ammonium bases. What effect could the fourth group have on the basicity? Since the third group lessens the basicity, we should expect the fourth group to still further diminish it. Let us see what are the facts: —

Volumes	Tetramethylammonium Hydroxide	Tetraethylammonium Hydroxide
	μ_v	μ_v
16	205	176
64	211	183
256	(213)	187

The fourth group increases the basicity to such an extent that the quaternary ammonium bases are not only stronger than the primary and secondary, but are to be ranked with the very strong bases, being nearly as strong as the alkali hydroxides themselves. The presence of four substituting groups in bases in general makes them very strongly basic. Take the weak bases, — phosphine, arsine, and stibine (PH_3, AsH_3, SbH_3). These compounds form derivatives which seem to be tetrasubstitution products of H_4POH, H_4AsOH, and H_4SbOH, in which the four hydrogen atoms are replaced by methyl groups. These compounds are tetramethylphosphonium hydroxide, tetramethylarsonium hydroxide, and tetramethylstibonium hydroxide, having the respective formulas: $(CH_3)_4POH$, $(CH_3)_4AsOH$, and $(CH_3)_4SbOH$. These are strongly basic substances, as will be seen from the following conductivity results taken from the work of Bredig:[1] —

Volumes	Tetramethylphosphonium Hydroxide	Tetramethylarsonium Hydroxide	Tetramethylstibonium Hydroxide
	μ_v	μ_v	μ_v
16	200	197	166
64	207	202	169
256	208	204	171

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[1] *Ztschr. phys. chem.* **13**, 301 (1894).

Constitution as conditioning Basicity. — The effect of constitution on basicity can be seen by comparing isomeric substances. Take propylamine and isopropylamine: —

Volumes	Propylamine	Isopropylamine
	μ_v	μ_v
8	12.3	13.0
32	23.9	25.7
128	44.7	47.1
256	59.6	62.3

Isopropylamine is a slightly stronger base than propylamine, but the difference is very slight.

There are, however, many cases known, as Bredig points out, of isomeric and metameric compounds which have very different strengths as bases. This shows that constitution often has a marked influence on the strength of bases, as we have seen that it has on the strength of acids.

The results contained in this chapter, like those of the earlier physical chemistry, are purely empirical. We know how certain elements and groups affect the strength of the acid or base into which they enter, and that the effect may depend upon the way in which these are combined with other substances in the molecule. We do not know, nor do we have any idea, why this is the case. Why does an oxygen atom increase the acidity of certain compounds, and diminish the acidity of others? and why does the presence of a nitro group affect the acidity quite differently in different positions? are questions to which we have absolutely no satisfactory answer.

The physical chemist of to-day, like the physical chemist of the earlier part of the nineteenth century, must be content for the time being with empirical results in certain directions. He, however, recognizes that this is but a necessary stage in the development of the subject, and in nowise regards it as final.

We have seen how great masses of empirically established facts have already been placed upon an exact physical and mathematical basis. The aim of the physical chemist in the future will be to extend and supplement these generalizations, which have already accomplished so much for the science of chemistry.

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